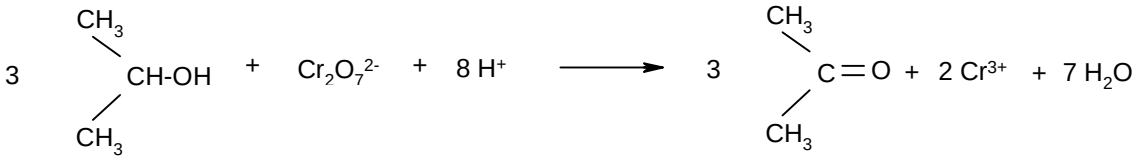
Kinetics: The Oxidation of an Alcohol by Dichromate Ion

INTRODUCTION

In this experiment you will learn to determine how the rate of a reaction is affected by changes in the reactant concentrations at a constant temperature. You will measure the rate of oxidation of isopropyl alcohol by dichromate ion in an acid solution. The rate of the oxidation is measured by following the disappearance of $Cr_2O_7^{2-}$, which has a bright yellow color, using a spectrophotometer. As the dichromate reacts, the Cr(VI) is reduced to Cr(III) which, although pale green in color, does not absorb at the same wavelength as the dichromate ion. All other reactants and products are colorless.

The balanced reaction is shown below.



isopropyl alcohol acetone

You will determine the order of the reaction with respect to each of the three reactants, and calculate the specific rate constant. This can be cleverly accomplished using only six experimental runs if you "flood" the system (add large, but known, excess amounts) with two of the three reactants. The two reagents in large excess remain *essentially* constant throughout the course of the oxidation so that an observed rate constant can be determined by monitoring only the concentrations of the third reactant with time. (The concentration of the third reactant, $\mathbf{Cr_2O_7^{2-}}$, will be followed spectrophotometrically since it is a colored species). In different runs of the experiment, we will use different concentrations of alcohol and acid (the reagents in excess) in order to observe how these concentrations affect the rate of the reaction.

The technique of "flooding" the system with all reagents but one is commonly used by kineticists and results in a pseudo-order reaction with respect to the limiting reagent. "Pseudo" is a prefix from the Greek word that means to deceive. In fact, you are tricking the system into a critical dependence on only one substance. This can be shown mathematically as follows. The general rate law for the oxidation of isopropyl alcohol (C_3H_7OH) with dichromate is:

$$\mathbf{rate = k[C_3H_7OH]^x[Cr_2O_7^{2-}]^y[H^+]^z}$$

If large excesses of C_3H_7OH and H^+ are present (relative to $[Cr_2O_7^{2-}]$), then the initial and final concentrations of these two species remain constant. As a rule-of-thumb, the limiting reagent should have a concentration 100 times less than the others. Since $[C_3H_7OH]$ and $[H^+]$ are relatively constant, they can be considered as part of the observed rate constant.

$$\mathbf{rate = k_{obs}[Cr_2O_7^{2-}]^y}$$

where $\mathbf{k_{obs} = k[C_3H_7OH]^x[H^+]^z}$

Thus, in some experiments you will be seeking data with which to calculate y and k_{obs}. In turn, variations in k_{obs} with $[C_3H_7OH]$ and $[H^+]$ will give you **x**, **z**, and **k**.

Spectrophotometry

For a review of the theory and technique of spectrophotometry see Appendix A. Appendix E and a General Chemistry textbook provide a review of kinetics.

The basic equation for measuring concentrations by spectrophotometry at a set wavelength may be stated as:

$$\mathbf{A} = \boldsymbol{\xi}\mathbf{bC} = \log\left(\frac{\mathbf{I_o}}{\mathbf{I}}\right) \qquad (1)$$

where
- **A** = absorbance
- $\mathbf{I_O}$ = intensity of light entering sample
- **I** = intensity of light passing through the sample
- $\boldsymbol{\xi}$ = molar absorptivity per molar concentration per each centimeter of light path length
- **b** = length of light path in sample (i.e., the diameter of your test tube)
- **c** = molar concentration of the colored substance

This is known as the Beer's Law. You should recognize that using one chromophore, or colored substance, and only one path length, the absorbance is directly proportional to dichromate concentration. Your readings of A at specific times will yield the concentration *vs* time data needed to determine the rate and rate law.

On most spectrophotometers it is more convenient to read percent transmittance, $I_O/I \times 100$, than to read A directly. This is because %T is a linear scale from 0 to 100, while A is a logarithmic scale from 0 to 2. Equation (2) shows the relationship between absorbance and percent transmission.

$$\mathbf{A} = 2 - \log(\%\mathbf{T}) = \log\left(\frac{100}{\%\mathbf{T}}\right) \qquad (2)$$

EXPERIMENTAL

The experimental part will be done in a cooperatively. Each person will be assigned into a group. At the end the measured data will be shared within each group. Data calculation and lab report, however, must be done individually.

Part I. Determination of λ_{max} for $Cr_2O_7^{2-}$ ion.

1. Turn on the spectrophotometer so that it can warm up for at least 20 minutes.

2. Select and clean a set of cuvettes to serve as blank and sample holders, respectively. Set the wavelength at 400nm. "zero" the spectrophotometer with the left knob when nothing is in the closed compartment. "100%" the spectrophotometer with the right knob when the cuvette is filled to the horizontal white line and it is in the closed compartment. Remember, whenever the wavelength is changed, the instrument must be "zero" and "100%" as described. It is not necessary to make these adjustments at fixed wavelength though it won't hurt to check them periodically. See Appendix A for more details.

3. In a 100-mL graduated cylinder add 1-mL of 0.0725M $K_2Cr_2O_7$ stock solution and dilute to the 100-mL mark with 3M H_2SO_4. CAUTION: Potassium dichromate ($K_2Cr_2O_7$) is a strong oxidizer and a poison and is known to cause cancer. Wear gloves and eye protection as it can be absorbed through the skin. A lab coat or apron is recommended. Sulfuric acid is both a poison and quite corrosive. The same personal protection requirements apply. Mix thoroughly and rinse a cuvette several times with small portions of this solution. Then fill the cuvette with the appropriate amount of diluted dichromate solution. Measure the %T of this solution from 400 nm to 500 nm at 10 nm increments. Examine your data then take more data on each side of the minimum of %T at 5 nm increments. Remember, each wavelength change must be accompanied by re-zeroing and "100%T" of the machine before taking the actual sample data. Do not use this solution in Part II.

4. Convert the %T readings to absorbances and plot A *vs* λ. Choose λ_{max} from the spectrum and set the spectrophotometer dial to this value for all remaining runs.

Part II. The Kinetic Data

1. Prepare seven clean cuvettes. Pipets should be used to dispense each of the following reagents.

3.00 M H_2SO_4
7.50 M isopropyl alcohol in water
deionized water
7.25×10^{-2} M $K_2Cr_2O_7$

For each run, the indicated volumes of sulfuric acid, isopropyl alcohol, and water should be added into one beaker while the dichromate in another.

Experimental Run	H_2SO_4 mL	C_3H_7OH mL	H_2O mL	$K_2Cr_2O_7$ mL
1	25.0	10.0	30.0	10.0
2	25.0	20.0	20.0	10.0
3	35.0	10.0	20.0	10.0
4	35.0	20.0	10.0	10.0
5	50.0	10.0	5.0	10.0
6	50.0	5.0	10.0	10.0

2. When ready, mix the two solutions, that will be time zero. Mix the solutions well, then fill one of the cuvettes with the mixture and begin recording %T as a function of time. Consider the following: if the run is proceeding very quickly (i.e., %T is changing rapidly), read %T and time quickly so sufficient data points are obtained before the dichromate is all consumed. If the run is slow, however, the time interval should be more widely spaced. As a start, take data every ten seconds for five minutes.

3. At the end of each run, do not discard the solution, save the sample by simply setting it aside for a later measurement of A_∞ which is the absorbance of the solution after the reaction has gone to completion.

4. Repeat procedure steps 2 and 3 for runs 2-6. You may find that one or more behaved unexpectedly, *i.e.*, reacting much too fast or not at all. If so, repeat that run.

5. When all six runs are finished, carefully measure $\%T_\infty$ for all the runs.

6. Place all of your discarded solutions into the properly labeled hazardous waste container in the fume hood.

DATA ANALYSIS

1. Your data table for each run should contain the following columns: time, %T, A, $(A - A_\infty)$, $\ln(A - A_\infty)$, and $1/(A - A_\infty)$ (relate this to Experiment 0, the tutorial exercise).

2. Make plots to check for zero, first, and second order with respect to the $Cr_2O_7^{2-}$ concentration (see Appendix E). This means plot $A - A_\infty$ vs. time, $\ln(A - A_\infty)$ vs. time, and $1/(A - A_\infty)$ vs. time. The linearity of the plot should be based on the R^2 value - the Pearson product moment correlation coefficient. Do this for ALL six runs. Question: If run 1 data, $(A - A_\infty)$ vs. time, yields a linear plot, should all the other runs also give a straight line when $(A - A_\infty)$ is plotted against time and why?

3. From the six linear graphs, use the least square method to find the values of k_{obs}. Formulate a table of k_{obs} values in conjunction with $[H^+]$ and $[C_3H_7OH]$. Calculate x and z. Using x, z, and k_{obs}, determine the value of the specific rate constant, k.

4. Finally, write the complete rate law for this reaction. That is one based on the actual k, x, y, and z and another, based on the rounded x and z.

Have you

1. wipe down all benchtops, including the sink, hood, and balance areas?
2. return all stock chemicals to their proper locations?
3. return all equipment to your drawer or general supply area?

4. lock your desk drawer?