

COBALT(III) KINETICS

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Introduction

Cobalt(III) complexes are excellent oxidizing agents. The standard reduction potential for the one electron reduction of $\text{Co}(\text{H}_2\text{O})_6^{3+}$ is 1.81 V, which is high enough to oxidize water to O_2 . $\text{CoW}_{12}\text{O}_{40}^{5-}$, the ion to be studied in this experiment, has a literature standard reduction potential of 1.00 V for the one electron reduction to $\text{CoW}_{12}\text{O}_{40}^{6-}$.² While this potential is considerably less than that of $\text{Co}(\text{H}_2\text{O})_6^{3+}$, this heteropoly ion is still a strong oxidizing agent.

The first step in an investigation into any reaction mechanism is to study the reaction kinetics. At a minimum, any proposed mechanism MUST agree with the experimentally determined rate law. A good mechanism will also explain changes to the rate or observed rate constant that result from changing reaction conditions. Although it is difficult (or even impossible) to prove a mechanism, any proposed mechanism that does not agree with an experimentally determined rate law is either wrong or incomplete.

In this experiment, we will study the reaction of $\text{CoW}_{12}\text{O}_{40}^{5-}$ with a reducing agent by monitoring the concentration of $\text{CoW}_{12}\text{O}_{40}^{5-}$ with UV-visible spectroscopy. The rate will be measured as a decrease in the concentration of $\text{CoW}_{12}\text{O}_{40}^{5-}$ over time, $-\text{d}[\text{CoW}_{12}\text{O}_{40}^{5-}]/\text{dt}$. For simplicity, we will designate the $\text{CoW}_{12}\text{O}_{40}^{5-}$ anion simply as Co(III) and the reductant as “R”. The general redox reaction between the heteropolyanion and a reducing agent can be described by the rate law:

$$v = -\frac{\text{d}[\text{CoW}_{12}\text{O}_{40}^{5-}]}{\text{dt}} = k_{rxn}[\text{Co(III)}]^a[\text{R}]^b \quad (1)$$

To simplify our study, we will perform the reaction under pseudo 1st order conditions. In pseudo 1st order kinetics, one of the reactants (in this case the reducing agent) is added in large excess (usually 10 fold excess or higher) so that the concentration of that reactant does not change during the experiment.

This DOES NOT mean that the reaction rate is unaffected by the concentration of the excess reactant.

It merely means that we add enough of one reactant so that we don't have to worry about its concentration changing during a specific experiment or rate determination. We can still change the concentration of the excess reactant (move from 10 to 15 fold excess) and see how that change affects the reaction rate and observed rate constant.

Because the excess reactant concentration does not change, it is often combined into the *observed* rate constant (k_{obs}) to simplify the rate law:

$$v = k_{obs}[\text{Co(III)}]^a \quad \text{where} \quad k_{obs} = k_{rxn}[\text{R}]^b \quad (2)$$

Under a given set of conditions, a reaction can have only one reaction order for each reactant. For relatively simple reactions, the reaction order (a or b in equation (1)) will be an integer between 0 and 2. This reaction order is often interpreted in terms of the *molecularity* of the reaction. In other words, the reaction order begins to describe the number of molecules involved in the mechanism at or before the rate

determining step. Fractional reaction orders often indicate that the mechanism is more complicated, or that it may involve equilibrium steps.

Equation (1) is a rate law that relates the change in concentration of one of the species (the reaction rate) to the concentrations of the reactants. The integrated form of the rate depends on the value of a ; that is, on the order of the reaction in $\text{CoW}_{12}\text{O}_{40}^{5-}$. Integrated forms of simple 0, 1st and 2nd order rate laws are compiled in Table 1 below.

Table 1. Integrated Rate Laws.

Order	Integrated Rate Law	Linear Plot	
0	$[\text{Co(III)}]_t = -k_{obs}t + [\text{Co(III)}]_o$	$[\text{Co(III)}]$ vs. t	(3)
1	$\ln[\text{Co(III)}]_t = -k_{obs}t + \ln[\text{Co(III)}]_o$	$\ln[\text{Co(III)}]$ vs. t	(4)
2	$\frac{1}{[\text{Co(III)}]_t} = k_{obs}t + \frac{1}{[\text{Co(III)}]_o}$	$\frac{1}{[\text{Co(III)}]}$ vs. t	(5)

The integrated form of the rate law usually relates the concentration of a reactant at any time ($[\text{Co(III)}]_t$) to the initial concentration ($[\text{Co(III)}]_o$) of that reactant and the rate constant (k_{obs}). This relationship changes substantially with the reaction order, as can be seen from the variety of integrated rate laws in the table. For simple reactions, the reaction order can be determined by fitting concentration vs. time data to one of the three integrated rate laws. A convenient way to do this is to plot the data from a single kinetics experiment (or set of experiments) in the three linear forms and then evaluate which of the three equations best describes that data. This is how you will treat your data in this experiment. Ideally, the plot is linear for the entire reaction, but in practice the plot may start deviating from linearity after the reaction is about 75% complete. A substantial advantage to using the linear form of the integrated rate law is that the slope of the line is equal to k_{obs} .

In this experiment the concentration of the oxidant is determined from the absorbance, A , of the ion at 388 nm. The product of the reaction (Co(II)) may also absorb light at this wavelength, and you may need to account for this. To determine if you should correct for the spectrum of the product, you will need to know how the absorbance by Co(II) at 388 nm and how that relates to the absorbance by any remaining Co(III). This can be accomplished with the following equation:

$$\text{Error} \approx \%C \times \frac{A_{\infty}}{A_o} \quad (6)$$

where

$$\%C = \frac{[\text{Co(II)}]_t}{[\text{Co(III)}]_o} \times 100\% = \left(1 - \frac{[\text{Co(III)}]_t}{[\text{Co(III)}]_o} \right) \times 100\% \approx \frac{A_o - A_t}{A_o} \quad (7)$$

$\%C$ is the percent of reactants that has been converted to products, A_{∞} is the absorbance of the product

(after having an “infinite” time to react, i.e. the spectrum of the final product mixture), and A_0 is the initial absorption. This ratio evaluates the relative importance of absorbance due to the reactants and products at any time during the reaction. As you can see from the equation, the error introduced by the product spectrum will be smallest at the beginning of the reaction (when mostly reactants are present) and largest will be largest towards the end of the reaction (when mostly products are present). You should evaluate the error due to Co(II) each of your experiments (a single kinetics experiment is commonly called a “run”). If the % error is higher than 10% for any kinetic run, you should correct that run the A_∞ absorbance. To do this, simply plot $(A - A_\infty)$ vs. t rather than A vs. t .

The order of the reaction in reductant (the value of b) can be determined by measuring k_{obs} as a function of reductant concentration for a constant concentration of $\text{CoW}_{12}\text{O}_{40}^{5-}$. The best way to do this is to measure k_{obs} using several concentrations of reductant. Remember that under pseudo 1st order conditions $[\text{R}]$ will not substantially change during a single run, but that pseudo 1st order conditions does not imply that the reaction is 0 order in $[\text{R}]$ under those conditions. Again, using a linear plot simplifies the data treatment and often helps limit the impact of small experimental errors. Recall from equation 2 that:

$$k_{obs} = k_{rxn}[\text{R}]^b \quad (8)$$

Taking the log of both sides yields:

$$\log(k_{obs}) = \log(k_{rxn}) + b \cdot \log([\text{R}]) \quad (9)$$

Therefore, a plot of $\log(k_{obs})$ vs. $\log([\text{R}])$ should yield a straight line with slope of b , the reaction order in reducing agent. Although the intercept of this line is related to k_{obs} , this is not the best way of determining its value.ⁱ Once the value for b is determined, each experiment provides a measurement of the rate constant. By simply substituting the values for $[\text{R}]$, b , and k_{obs} back into equation 8, k_{rxn} can be determined for each run. Averaging all the determined values for k_{rxn} gives a much more accurate value for the rate constant.

Mechanism

Oxidation-reduction reactions of transition metal complexes are typically classified as either inner-sphere or outer-sphere. In the case of the inner-sphere mechanism, the electron is usually transferred along with the transfer of an atom or group (e.g. a Cl^- ligand). Outer sphere mechanisms occur by passing one or more electrons directly through space with no actual “contact” between the electron donor and acceptor. In order for this transfer to occur, however, the two reacting species must come into very close proximity. In $\text{CoW}_{12}\text{O}_{40}^{5-}$, the Co(III) is buried inside the tungstate tetrahedral. This means that Co(III) does not have any transferable groups and cannot have any atom or group transferred to it, so we would expect the mechanism to be outer-sphere.

ⁱ The line that arises from equation 9 generally has data relatively far from the y intercept. This means that very small errors in the data from the line are amplified when extrapolated to $x = 0$. So, even though the value for the slope may be very good, there may be large errors in the intercept simply because the data is collected so far from the intercept.

In the case of an outer-sphere mechanism between two anions, the rate is often dependent on the concentration of cations, especially the concentration of alkali metal cations. The cations facilitate the reaction by providing a means to bring the two like-charged anions together to permit electron transfer. In order to prevent complications due to cation effects, all the reactions will be run in a solution with a large and constant alkali metal ion concentration.

Many reaction rates can also vary with hydronium ion (H^+ or H_3O^+) concentration. If the reducing agent is a weak acid or the salt of a weak acid, it could be present in both the neutral and anionic forms. The rate of reaction of the $\text{CoW}_{12}\text{O}_{40}^{5-}$ with each of these will not be the same because of the difference in charge. Thus, if both forms are present, there will be two competing processes that lead to the same product. One way to eliminate this problem is to use a large enough H^+ concentration so that essentially all the reducing agent is present as the neutral molecule.

Systems to be Studied

In these experiments, the reducing agent will be present in large excess. The solvent in each case is an aqueous solution containing 1 M Na^+ and, where necessary, added acid in the form of HCl. It is possible to use HCl and NaCl because the experiment is being carried out at room temperature. At high temperatures the $\text{CoW}_{12}\text{O}_{40}^{5-}$ is a strong enough oxidizing agent to convert Cl^- to Cl_2 . Thus for high temperature studies, a nonoxidizable anion must be used.

The kinetics of the reaction of $\text{CoW}_{12}\text{O}_{40}^{5-}$ with several reducing agents have been previously studied, including those investigated here.³⁻⁵ The reaction with SCN^- has been shown to be independent of $[\text{H}^+]$ in the range 0.10 to 1.00 M. It was also shown that the reaction mole ratio of SCN^- to $\text{CoW}_{12}\text{O}_{40}^{5-}$ is 1 to 1.³ When oxidized, SCN^- forms $(\text{SCN})_2$ which, in the presence of excess SCN^- , is converted to $(\text{SCN})_3^-$. The reaction with HNO_2 has also been shown to be independent of $[\text{H}^+]$ in the range 0.10 to 1.00 M. It was also shown that the reaction mole ratio of HNO_2 to $\text{CoW}_{12}\text{O}_{40}^{5-}$ is 1 to 2.⁴ A dilute solution of HNO_2 is produced by dissolving NaNO_2 (s) in 0.1 M acid. When oxidized, HNO_2 forms NO_3^- .

Table 2. Reaction Details of the Two Systems.

Reducing Agent	Starting Material	Mass of starting material	Solvent
HNO_2	NaNO_2 (s)	55 mg	1.0 M NaCl, 0.1 M HCl
SCN^-	NaSCN (s)	97 mg	1.0 M NaNO_3

Procedure

You will be assigned one of the two systems in Table 2. You will need about 300 mL of the solvent. Prepare 100 mL of a $\text{CoW}_{12}\text{O}_{40}^{5-}$ solution by dissolving 0.35 g of $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}$ in 100 mL of the solvent given. The concentration will be approximately 4×10^{-4} M. If there is any insoluble material, filter the solution before you use it. Measure the absorbance at 388 nm; this value should be between 0.30 and 0.50. If the absorbance is lower, add more solid $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}$. If the absorbance is higher, pour some of your solution out and add more solvent. Once you have your final solution ready, collect a full spectrum from 350-900 nm.

The actual concentration of $\text{CoW}_{12}\text{O}_{40}^{5-}$ can be calculated from your absorbance measurement using Beer's law (the molar absorptivity at 388 nm is $1150 \text{ L mol}^{-1} \text{ cm}^{-1}$). The $\text{CoW}_{12}\text{O}_{40}^{5-}$ concentration in the solution used for each kinetics run will be one-half this value because the solution is diluted with an equal volume of the reducing agent solution.

For the system assigned from Table 2, prepare 100 mL of your stock reducing agent solution (use a 100 mL volumetric flask). This solution will be the most concentrated solution for your kinetics experiments. You will also dilute this solution to prepare the reducing agent solutions of lower concentration (use 25 mL volumetric flasks and volumetric pipettes). Dilution directions are in Table 3. The best results will be obtained when the other four solutions are approximately evenly spaced through the concentration range for your reducing agent. Be sure to mix the solutions thoroughly before using them.

Table 3. Dilution of Stock Reducing Agent Solution

Use a 25 mL volumetric flask and volumetric pipets.

Volume of Stock Solution	Diluted to
20 mL	25 mL
15 mL	25 mL
10 mL	25 mL
5 mL	25 mL

Each of the 5 solutions should be tested a minimum of three times (at least 15 runs total). Your reference solution should contain only your solvent. For the most concentrated reducing agent sample, monitor the absorbance for 6 minutes, printing absorbance measurements every 10 seconds (see spectrometer instructions at the end of the experiment). For all other samples, monitor the absorbance for at least 90 seconds taking absorbance every 2 seconds.

Before starting a run, autozero the spectrometer with your solvent in the sample holder (cuvette or sipper). To prepare a sample, pipette 5 mL of the $\text{CoW}_{12}\text{O}_{40}^{5-}$ solution into a small beaker. Pipette 5 mL of the reducing agent solution into a second beaker. Quickly mix the solutions by pouring them back and forth between the beakers 3-5 times. Carefully pour the solution into the cuvette (or sip through the sipper),

and begin measurements as soon as possible. Note that the reaction proceeds quickly and that useful measurements generally will be obtained within the first few minutes of mixing. **For runs with the most concentrated solution, save the solution not placed in the spectrometer.** At the conclusion of all the runs, the reaction should be complete and the solution should be blue. Measure the absorbance of this solution at 388 nm; this is A_{∞} . The A_{∞} value should be the same for these runs but you may want to measure all three to ensure that you have a reproducible value for A_{∞} . Additionally, collect a complete spectrum for your A_{∞} solution from 350-900 nm (this is the spectrum of the Co(II) product).

Reproducibility is important for this experiment! You will want to examine your runs to make sure that each set of runs has similar rates. To do this, simply subtract the last Absorbance value from the first for each run. If your runs with a given solution are reproducible, this change per run should be similar.

**Reproducibility
is Important!**

Procedure Summary

1. Reaction order for $\text{CoW}_{12}\text{O}_{40}^{5-}$.

- use highest concentration of your reducing agent
- monitor each run for 6 minutes, collecting data every 10 seconds
- do **at least** 3 runs

2. Reaction order for reducing agent

- monitor each run for 90 seconds, collecting data every 2 seconds
- do **at least** 3 runs per reducing agent concentration (you do not need to repeat the runs from part 1 above, but will want to plot only the first 90 seconds to be consistent with the other experiments)

Calculations

Determine the order of the reaction in $\text{CoW}_{12}\text{O}_{40}^{5-}$. For this determination, use only your runs at high reductant concentration (the longer runs). Each run will need to be plotted 4 different ways. For convenience, you may plot all three data sets for each type of plot on the same set of axes.

Figure 1: Absorbance vs. time or $(A - A_{\infty})$ vs. time

Figure 2: 0 order integrated rate law plot (with linear fits, line equation, and R or R^2 values)

Figure 3: 1st order integrated rate law plot (with linear fits, line equation, and R or R^2 values)

Figure 4: 2nd order integrated rate law plot (with linear fits, line equation, and R or R^2 values)

One of the integrated rate law plots should be very linear – this is most easily evaluated by fitting each plot with a line. The reaction order for Co(III) corresponds to the best fit of the three types of plots; the “wrong” plots will show some degree of curvature.

Determine the order of the reaction in reducing agent. Once you have determined the reaction order for Co(III), you can then evaluate all of your kinetic data using appropriate integrated rate law equation. As long as all of your kinetic runs are linear using the appropriate rate law plot, it is reasonably safe to assume that the reaction order remains constant throughout the concentration range you are studying. For each run, the slope of the best fit line is the k_{obs} value for that run. **You do not need to hand in plots for**

all 15 runs. Rather, prepare a table showing the average value and standard deviation of k_{obs} at each [R]. To determine the reaction order in reducing agent, prepare a plot of $\log k_{obs}$ vs. $\log [R]$ using your average value for each k_{obs} . The slope of this line will be the reaction order in [R] (in most cases this is rounded to the nearest whole number when the reaction order is reported).

Determine the rate constant (k_{rxn}) The rate constant can now be extracted directly from each measurement of k_{obs} by substituting the appropriate values into equation (6) and solving for k_{rxn} . For each run, determine the measured value for k ; report only the average value for all your kinetic runs and the standard deviation.

Discussion Questions

1. Explain what the reaction orders mean in terms of the molecularity of the rate determining step, and why this information is important to the mechanism.
2. This reaction can be understood in terms of an Eigen-Wilkins type mechanism, invoking an “encounter complex” intermediate. Using this general mechanism, derive the rate law for this reaction. Make no assumptions about the relative rates of the steps, other than that the first step is a rapid equilibrium (i.e. the equilibrium is always satisfied).
3. How does this general mechanism simplify into your rate law? What does this tell you about the upper and/or lower limits for the equilibrium constant and the rate constant in this reaction? To neglect a term in the denominator, assume that it must be no more than 1% of the other terms.
4. Is this reaction likely to be an inner sphere or outer sphere electron transfer? Justify your choice based on both the nature of the complexes AND the kinetic evidence.

References

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3. Ayoko, G.A.; Olatunji, M.A. *Indian J. Chem.* **1984**, 23A, 769.
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Instructions for the Hitachi UV-Vis Spectrophotometer (kinetics experiment)

1. From the MAIN MENU, select the TIME SCAN option.
2. The DATA MODE should be set to ABS.
3. In the TEST SETUP menu, set the wavelength the value in the lab experiment, the UP SCALE and LO SCALE to reasonable values for this experiment, and SCAN TIME to the total time for that particular run and solvent (usually 90 s or 240 s).
4. The FORWARD key takes you to the TIME SCAN screen.
5. Fill the reference cuvette with some of your blank solution (solvent).
6. IMMEDIATELY PRIOR TO EACH RUN, AUTOZERO the spectrometer with a cuvette filled with your solvent.
7. Quickly mix your sample solution, fill your sample cuvette, and insert into the sample cuvette holder.
8. Press the START key to initiate data collection.
9. After the time curve has been completed, the complete curve will be displayed on the screen. From the options at the bottom of the screen, select RECALC (option 7), press ENTER, then select PRINT DATA (option 2), then the ENTER key. Now select TIME (option 3) and set the time to the value entered in step 3 (in seconds) and press ENTER. Now select INTERVAL (option 4), press ENTER, and set the time interval to the interval between data points that you want to print (usually either 2 or 4 s). Finally {if no one else is printing}, select PRINT START (option 1), press ENTER, and your absorbance versus time data will print.
10. After printing the data, use the RESUME key on the printer to remove your data from the printer. The data should be in an absorbance vs. time format with the interval you selected in 9 as the time difference between points.
11. Repeat steps 6 through 10 for each kinetics run.
12. Finally, clean all your cuvettes (sample and reference) with DI water. Then press the MAIN MENU key.