

The Kinetics of Aquation of the *Trans*-dichlorobis (ethylenediamine)-Cobalt(III) ion¹

Purpose: Determine the order, rate constant, activation energy, and pre-exponential factor for the ligand exchange reaction of a water for a chloride ion in *trans*-dichlorobis (ethylenediamine)-cobalt(III) ion.

Introduction

There are two questions of general importance when considering all chemical reactions. The first question concerns the feasibility of carrying out a reaction, that is determining the equilibrium position of a reaction. Chemical thermodynamics deals with the position of equilibrium. The second question concerns how fast the equilibrium position is established. This area is called chemical kinetics. Together the questions are: how far and how fast?

Numerous rules and concepts can aid the prediction of whether a particular reaction will occur (thermodynamic considerations). Some of the following are used in the study of chemistry: activity series, rules of exchange reactions, equilibrium constants, solubility product constants, oxidation-reduction potentials, and free energies of reactions.

However, the prediction of how fast a chemical reaction will occur is much more difficult. The ultimate factor controlling the rate of reaction involves the mechanism of reaction, which involves a detailed time picture of exactly how the molecules and atoms are interacting during the course of the reaction.

The Rate Expression

The rate expression for a chemical reaction is based on data obtained from a kinetic study conducted in the laboratory. From the experimental rate expression, a detailed mechanism for the reaction can be developed. In general, the rate of a chemical reaction



will be given by

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} \quad 2$$

where the brackets refer to concentrations generally in moles liter⁻¹. The rate expression frequently has the form

$$\text{rate} = k [A]^n [B]^m \quad 3$$

where k is the rate constant, $[A]$ is the concentration of A and $[B]$ is the concentration of B in moles liter⁻¹ and n and m are exponents called the reaction orders. There is no necessary relation between the values of the exponents n and m and the coefficients a and b in equation 1. This situation exists because the chemical equation gives no information about the mechanism of the reaction and the values of n and m depend on the mechanism. For example, the transformation of $A + B$ into products may proceed via more than one step.

In this experiment the rate expression for a chemical reaction will be determined, as well as the temperature dependence of the rate constant.

First-Order Rate Expression

One of the simplest types of rate expression is first-order in one of the reactants:

$$\text{rate} = -\frac{d[A]}{dt} = k [A] \quad 4$$

For equation 1 this would be the case if $n = 1$ and $m = 0$ or if $[B]^m$ is kept constant and included in k . This could be done experimentally by having B in great excess, in which case, the overall concentration change of B during the course of the reaction would be negligible. The process is then said to be first-order in A. The integrated rate expression is,

$$\ln \frac{[A]}{[A]_0} = -kt \text{ or } \ln [A] = -kt + \ln [A]_0 \quad 5$$

where $[A]_0$ is the initial concentration A at time zero and $[A]$ is the concentration at any time, t . The half-life of a chemical reaction is the time required for one-half of the reactant that was present at the start of a given time period to react. A first-order reaction has a constant half-time, $t_{1/2}$, since:

$$\ln \frac{[A]_{0/2}}{[A]_0} = -\ln 2 = -k t_{1/2} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k} \quad 6$$

Second-Order Rate Expression

If $n=2$ and $m=0$ or $[B]^m$ is held constant in equation 3,

$$\text{rate} = -\frac{d[A]}{dt} = k [A]^2 \quad 7$$

the reaction is second-order in A and integration of equation 7 gives:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k t \quad 8$$

The half-life for a second-order reaction is found from

$$\frac{1}{([A]_{0/2})} - \frac{1}{[A]_0} = k t_{1/2} \quad \text{or} \quad t_{1/2} = \frac{1}{[A]_0 k} \quad 9$$

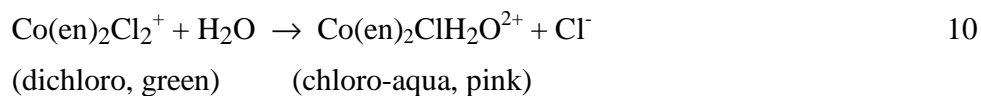
Determining the Reaction Order

To determine the order of a reaction, concentration verses time measurements are collected in the laboratory, and the data are plotted. According to equation 5, for a first-order reaction a plot of $\ln[A]/[A]_0$ verses t should yield a straight line. According to equation 8, for a second-order reaction a plot of $1/[A]$ verses t should yield a straight line.

The Reaction To Be Studied

Trans-dichloro-bis-ethylenediamine cobalt (III) ion, $\text{Co(en)}_2\text{Cl}_2^+$, is a complex ion that forms a green solution when dissolved in water. Ethylenediamine, here symbolized as "en," is $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$. Ethylenediamine is a bidentate ligand, which means that the cobalt ion in this complex has a coordination number of six. In solution, a water molecule may replace one of the Cl^- ions in this complex, giving a mixture of *cis*- and *trans*- $\text{Co(en)}_2\text{ClH}_2\text{O}^{2+}$, which forms a

pink solution. The purpose of this experiment is to investigate the kinetics of this aquation reaction:



The forward reaction may be expressed by the rate law

$$-\frac{d[\text{Co(en)}_2\text{Cl}_2^+]}{dt} = k [\text{Co(en)}_2\text{Cl}_2^+]^n \quad 11$$

where k is the rate constant, and n is the apparent order of the reaction. One might expect the concentration of H_2O to enter into the rate expression. Since this experiment is done in dilute aqueous solution, the concentration of water is large (55 M) and very nearly constant, so any dependence on $[\text{H}_2\text{O}]$ is incorporated into the constant k . The reverse reaction can be disregarded under the conditions in this laboratory.

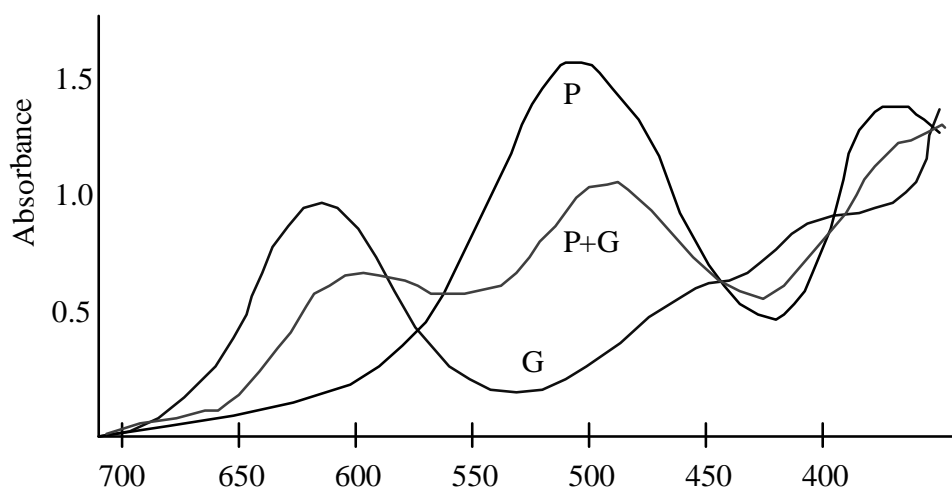


Figure 1.

P: Spectrum of an aqueous solution of $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}_2^+$. This solution is pink because it absorbs strongly in the green region.

G: Spectrum of an aqueous solution of $\text{Co(en)}_2\text{Cl}_2^+$. This solution is green because it absorbs strongly in the red and blue regions.

P+G: Spectrum of an aqueous solution of an aqueous mixture of the two species in equal concentrations.

Absorbance Measurements

The progress of the reaction is observed spectrophotometrically. The absorbance spectra of the dichloro and chloro-aqua complexes and a mixture of the two is shown schematically in Figure 1.

The concentrations of dichloro, $[\text{M-Cl}]$, and chloro-aqua, $[\text{M-H}_2\text{O}]$, forms are related to the absorbance, A , by the Lambert-Beer law. The absorbance of the solution is just the sum of the absorbances of the two species:

$$A = A_{\text{M-Cl}} + A_{\text{M-H}_2\text{O}} \quad 12$$

where the absorbance of each species is:

$$A_{\text{M-Cl}} = a_{\text{M-Cl}} \ell [\text{M-Cl}] \quad \text{and} \quad A_{\text{M-H}_2\text{O}} = a_{\text{M-H}_2\text{O}} \ell [\text{M-H}_2\text{O}]$$

where a is the molar absorption coefficient, ℓ the length of the optical path within the solution, and $[\text{M-Cl}]$ and $[\text{M-H}_2\text{O}]$ are the concentrations. (Please note that $[A]$, in brackets, is the concentration of species A , while A , without brackets, is the absorbance of the solution.) Within the visible region, the spectra of the dichloro and the aqua forms are distinctly different, but there is not a single maximum, free from overlap with other absorptions, that may be used for spectrophotometric analysis. To be able to follow the reaction progress at one wavelength, the following property of the stoichiometry of this reaction is used:

$$[\text{M-H}_2\text{O}] = [\text{M-Cl}]_0 - [\text{M-Cl}] \quad 13$$

From equations 12 and 13 the following relation can be derived:

$$\frac{[\text{M-Cl}]}{[\text{M-Cl}]_0} = \frac{A_t - A_\infty}{A_0 - A_\infty} \quad 14$$

where $[\text{M-Cl}]$ is the concentration at time t ; $[\text{M-Cl}]_0$ is the concentration at $t=0$; A_t is the absorbance at time t ; A_0 the absorbance at time $t=0$; and A_∞ is the absorbance after the reaction has gone to completion. Absorbances are for the reaction mixture composed of dichloro and chloro-aqua forms in solution.

Equation 14 eliminates the necessity of determining molar absorption coefficients and possible error in the initial concentration of the dichloro compound resulting from initiation of the reaction before the sample completely dissolves. Plots of $\ln[\text{M-Cl}]/[\text{M-Cl}]_0$ or alternatively $1/([\text{M-Cl}]/[\text{M-Cl}]_0)$ will verify the reaction order.

Determination of the Activation Energy

The second part of the exercise is the determination of the activation energy of the reaction. The rate constant for a reaction is related to the energy of activation, E_a , by the equation

$$k = A e^{-E_a/RT} \quad 15$$

where A , the pre-exponential factor, is a constant characteristic of the reaction, R is the gas constant, and T is the absolute temperature. By taking the logarithm of both sides, we obtain:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A \quad 16$$

Thus if you determine the rate constant for the aquation of $\text{trans-Co(en)}_2\text{Cl}_2^+$ at several different temperatures, you can make a plot of $\ln k$ against $1/T$. A straight line drawn through the points should have a slope of $-E_a/R$, and a determination of the slope permits a calculation of E_a . The intercept is used to calculate the pre-exponential factor.

Because the rate constant can be readily calculated from the half-time, $t_{1/2} = \ln 2/k$, a determination of the half-time is equivalent to a determination of the rate constant. Show that a plot of $\ln t_{1/2}$ versus $1/T$ would have a slope of E_a/R . Also determine the relationship of the pre-exponential factor to the intercept of this plot. The experimental procedure is to determine the half-time for several different temperatures.

Procedure

Part I. Determining the Visible Absorption Spectra of the Reactant and Product

The instructions for using the Ocean Optics Diode Array spectrophotometer are at the end of this manual. The $\text{Co(en)}_2\text{Cl}_2^+$ complex is available as the chloride salt, $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$. Determine the spectrum of a fresh cold dilute solution of $\text{Co(en)}_2\text{Cl}_2^+$ (make sure the water is cold before mixing with the solid complex to delay hydrolysis). Determine the spectrum of a hydrolyzed solution, which is $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$. The concentration is not important to determine the spectra. Choose an appropriate wavelength for the analysis by reference to your spectra and Figure 1.

Part II. Determining the Reaction Order

A time-course kinetic run will be done using a Spectronic 20 set to the wavelength you chose. Since both of the complexes in the reaction absorb throughout the visible region, the absorbance remains rather high during the entire course of the reaction. To yield better accuracy and precision in your measurements, it is best to use the initial solution at time zero to set 100%, rather than a pure water blank. This procedure will expand the scale of the spectrophotometer.

A suitable initial concentration range for the kinetic runs is 0.01–0.015 M. Make sure to do all solution preparation calculations before you come to lab. Measure absorbance versus time data for the hydration at 55°C in a thermostated bath. Use a test tube, clamped in the bath for a reaction vessel. Use a volume of 25 mL. Before adding the complex to the test tube, make sure the water in the test tube is at the bath temperature. Take aliquots from the solution in the water bath and determine the absorbance in the spectrophotometer every 1 to 2 minutes. Return the aliquot to the test tube in the bath, so that you don't run out of solution.

Calculations

Plot the data as discussed above, determine the reaction order and calculate the rate constant. Include both your first-order and second-order plot. Use least-squares curve fitting to determine the slope, rate constant, and the uncertainty in the rate constant.

Part III. Determination of the Activation Energy

The half-time of the reaction may be measured without the use of a spectrophotometer by comparing the color of the reaction to a reference made from a 50:50 mixture of the unhydrolyzed dichloro complex and the hydrolyzed chloro-aqua complex. This color reference is possible since at temperatures close to 0°C, a water solution of $\text{Co(en)}_2\text{Cl}_2^+$ undergoes no appreciable aquation. A solution of the hydrolyzed chloro-aqua complex can be easily prepared by placing a solution of the dichloro complex in a beaker of hot water for 5 to 10 minutes or by using the final solution from Part II. The design of the experiment is up to you. You are to determine the activation energy and the pre-exponential factor. This determination will probably require about five different temperature measurements. A suitable temperature range for the rate measurements is approximately 50°–85°C. Make sure the concentrations in each run match your color reference fairly accurately ($\pm 3\%$). Do the initial concentrations for each run have to be exactly the same? It is essential that strict temperature control be maintained: place, thusly, a water-filled test tube in a heated water bath, and allow it to reach the temperature of the bath before adding the $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$.

Calculations

Plot the data as discussed above, determine the activation energy and the pre-exponential factor from the slope and intercept of the straight line. Use least-squares curve fitting to determine the values and the propagated uncertainties.

Report

In the Introduction, describe the experiment and the expected results in a few sentences. For the Theory Section, just reference this write-up, but include the requested derivation that starts with Eq. 16; show that a plot of $\ln t_{1/2}$ versus $1/T$ would have a slope of E_a/R and determine the relationship of the pre-exponential factor to the intercept of the plot. For the Procedure Section, just reference this write-up. For the Results Section, provide the data in a tabular format, including all information necessary to repeat your calculations. Attach all three of your graphs. Report the order of the reaction, the rate constant at 55°C, the activation energy, and pre-exponential factor. Include any slopes and intercepts determined by curve fitting and the uncertainties in the quantities. Remember to use propagation of error rules in presenting the standard deviations in the final results. Discuss the chemical significance of the results. In other words, state why these results are useful and important. Discuss why someone might need to do a study of this type. Are the results for this system unusual or do they fall within the normal range of similar results for other systems? Answer the question in the procedure section of Part III (do the initial concentrations for each run have to be exactly the same?).

References

1. This lab write-up contains excerpts from the following sources:
 - a) W. L. Jolly, *Encounters in Experimental Chemistry*, Harcourt, Brace, and Jovanovich, New York, 1972.
 - b) R. E. Davis, D. S. Page, "The Kinetics of the Hydrolysis of Sodium Borohydride", in *Modular Laboratory Program in Chemistry*, KINE-070, Willard Grant, Boston, 1972.
 - c) The Harvard (summer school) *General Chemistry laboratory manual*, 1979.
 - d) U. A. Hofacker, *Chemical Experimentation*, Freeman, San Francisco, CA., 1972. Exercise 14.

Alternate Work

If the *cis*- complex is available, the kinetics of the *cis-trans* isomerization, in methanol solution, may be studied. Conditions and procedures, mentioned above, may be used for the *cis-trans* isomerization as well.