On the Cobalt Ammine Complex: low percentage yield and surprising rate constants

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ABSTRACT: The experiments detailed in this report center around the synthesis and purification of a Cobalt ammine (to analyze its percentage yield), as well as a reaction between this complex and the nitrite ion, NO_2^- (to analyze its reaction mechanism and kinetics). These experiments' findings can give key insights into how future experiments can be run efficiently and safely. For the first experiment, the limiting reagent in the synthesis of aquapentaammine cobalt nitrate is the cobalt complex—the theoretical yield in the experiment was 4.42g, and 0.974 g of the recrystallized and purified product was yielded, giving a yield percentage of 22.6%. For the reaction between the cobalt and the nitrite ion, we found the rate constant for both the initial ligand exchange and the ligand isomerization through the utilization of Beer' Law. The initial ligand exchange has a reaction rate constant k = 2.27 M^{-2} min^{-1} and the isomerization, k = 0.99 M^{-2} min^{-1}.

The topic of this paper centers around the cobalt ammine complex and its kinetic properties. In conducting these two experiments, we hoped to ascertain a **percent yield** for its synthesis and understand the **kinetics** behind one key chemical reaction between it and the nitrite ion.

Such topics are important because they are crucial to understanding the fundamental
underpinnings of this complex.

Figure 1a: the cobalt nitrate complex before hydration

In particular, cobalt complexes are an "essential metal" useful for imaging, and therapy, with lower toxicity and greater diversity of use than other metal complexes.[6] By understanding more about **percent yield**, one can better prepare for experiments and further research. By understanding more about this complex's **kinetics**, researchers, manufacturers, and engineers alike can manipulate the reaction to create more efficient reactions, getting the most product with the least amount of waste.

In calculating **percent yield**, chemistry principles tell us that a certain amount of product is *possible* if the reaction proceeds without any disturbances and the limiting reactant is able to react completely.[1] The *actual* mass of the complex after synthesis divided by the theoretical mass is

the **percent yield.** Steps such as purification and separation will undoubtedly lower one's percent yield because some product may be lost in the process. Other things may also lower percent yield, such as the purity of the starting compound, slow reaction rates, or decomposition.[2] Higher yields—resulting in a percent yield larger than 100%—are only possible if there are impurities in the final product. Many chemistry courses have utilized the formation of the cobalt ammine in studies on kinetics and purification, from Dartmouth College to Macalester and SUNY-Oneonta.[3,4]

In truth, cobalt ammines have been extensively studied since 1798.[7] Our experiments will simply quantify the percent yield once more through the synthesis and purification of the complex; given the pre-existing literature, it is hypothesized that the percent yield is around 40%.

The other experiment detailed in this report revolves around the **kinetics** of reaction between the cobalt complex and the nitrite ion. Many other studies have investigated the kinetics of the cobalt complex in conjunction with other compounds as well. The theory underlying Dartmouth College's CHEM 6 lab is the idea of conducting experiments to determine a pseudo-first order rate constant, given the rate law (Figure 1).[7]

$$\text{Rate} = k\,[Co(NH_3)_5(H_2O)_3+]\,[NO_2^-]\,[HNO_2]$$

Figure 1: rate law of the reaction between the cobalt complex and the nitrite ion, determined to be first-order with respect to each compound.[7]

One can then use this information to determine the actual rate constant for the steps in the reaction, employing differences in absorption spectra among the two isomers and the starting complex ion alongside Beer's Law. Given the pre-existing literature, it is hypothesized that both rate constants to be around 1.25 M^{-2} min^{-1}. It is difficult to estimate rate constants, same with percent yield, using only chemistry theory.

One now turns to the **methods** of the two experiments. In examining the **percent yield**, one simply needs to synthesize the complex and then compare the resulting mass to the predicted mass. The experimental design for the cobalt complex is a bit more complicated than this since there are many steps and reagents to get the final product, but the underlying principles are the same. The compound is further purified so impurities don't affect the percent yield. The entire protocol is laid out in the lab manual.

$$Yield = \frac{Actual}{Theoretical} x100$$

$$Yield = \frac{7.02}{10.22} x100$$
$$= 68.6\%$$

Figure 2: sample calculation for percent yield

For the **first experiment,** it is found that the limiting reagent is the cobalt complex $CO(NO_3)_2(H_2O)_6$. By examining the stoichiometry of this limiting reagent and the final product, it is calculated that the theoretical yield is 4.42g. After conducting

the experiment and weighing the final products, the crude product was found to be 1.39g, making the yield of the crude product 32.2%. The recrystallized product was 0.974g, making the purified yield 22.6%.

In examining the **kinetics** of the reaction, a combination of spectroscopy, coordination complex chemistry, and kinetics theory was used. There are two main steps in the reaction. The starting complex goes to an intermediary step (the nitro complex) and ends with the nitrito complex. Since each complex has a different color, experimenters were able to use absorption and Beer's Law to calculate the rate constants (Figure 3). The experiment simply involved setting up multiple solutions and measuring their absorbance every 3 minutes until the reaction is complete or has reached equilibrium. The protocol, same as with the first experiment, can be found in the CHEM 6 lab manual.

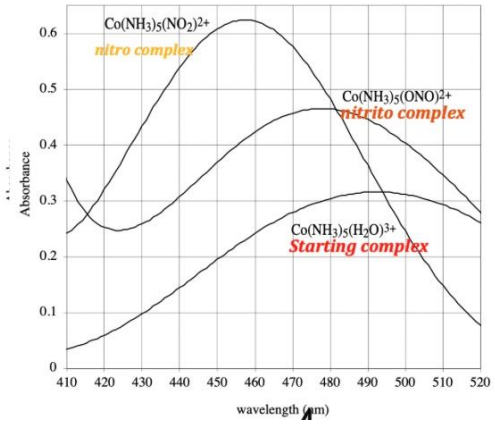

Figure 3: the max absorbance for each complex can be found at different wavelengths, and thus the different colors of the solution can give us insight on the concentration of the complex.[7]

For the **second experiment,** experimenters measured absorbance vs. time for the two-step reaction. Since the pseudo-first order reaction was used to determine the rate constant, $\ln[(A-A_\infty)/(A_0-A_\infty)]$ was graphed for both steps, the slope of which would become k' and can be plugged back into the rate law equation to determine k for the respective step (Figure 4). The reaction rate constant for the initial ligand exchange is k = 2.27 $M^{-2}\,min^{-1}$ and the isomerization, k = 0.99 $M^{-2}\,min^{-1}$.

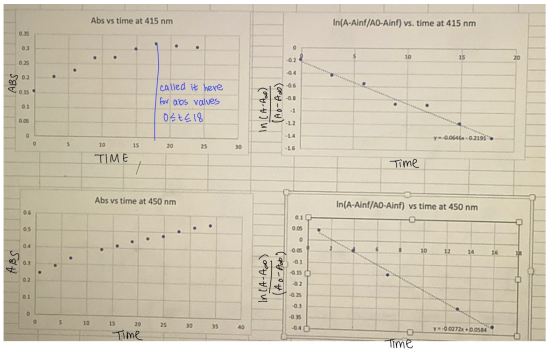

Figure 4: graphs of absorbance vs time and $\ln[(A-A_\infty)/(A_0-A_\infty)]$ vs time for the kinetics experiment. A best fit line was used to get the slope, - k'. A note for abs vs time at 415 nm shows which data points were used for the initial ligand exchange.

For the first experiment, the **percent yield** is quite low, at 22.6%. The previous hypothesis is thus rejected, which placed percent yield around 40%. Though 100% is very unusual for percent yield as well, optimal percent yields are "the higher the better", and previous CHEM 5 labs at Dartmouth yielded percent yields anywhere between 50-80%. Different experimental errors could have led to this drastically low yield, such as losing parts of the sample while transferring between vials or while weighing, unideal reaction settings leading to the reaction not fully terminating or

completing, or even losing some of the complex before the reaction even started but after it was weighed. Conducting a few more experiments will confirm whether the percent yield is indeed 22.6% (recrystallized) or not.

The **kinetics** of the isomerization is close to the hypothesized value, but the kinetics of the ligand exchange is larger than hypothesized. The initial ligand exchange having a larger rate constant is consistent with our knowledge of the reaction, given that the isomer is kinetically favored and can form quickly as the first step. The second step's isomer that is the final product is thermodynamically favored and more stable. This experiment's results are thus accepted. Having more data points could make the rate constant more accurate, as could doing the experiment a couple more times or pooling the class's data, should we be on-campus.

In conclusion, these two experiments center around the synthesis and purification of a Cobalt ammine as well as a reaction between this complex and the nitrite ion, NO_2^- . We found the percent yield of synthesizing a cobalt complex from cobalt nitrate and also the reaction rate constants for the two steps of the overall reaction between the cobalt complex and the nitrite ion. These findings contribute to the large network of literature already available on cobalt complexes, and give insight into the chemical nature of the complex and how researchers might manipulate it to yield better, more productive results. In analyzing the kinetics of the reaction, for example, one could figure out how to maximize output and create more cost-effective experiments and procedures for manufacturing.

References

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