Title: Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes: Rate of Decarboxylation of the Bis(carbonato)bis (pyridine)cobaltate(III) complex ion in Aqueous Pyridine Buffer Solutions
Devin Lubin

Abstract: The synthesis of the metal coordination was first prepared by dissolving $Na_3[Co(CO_3)_3]$ •$3H_2O$ in aqueous sodium bicarbonate. The reaction of these green solutions with excess pyridine was found to produce a pale blue, moisture-sensitive hydrate and then as the purple crystalline salt $K[Co(py)_2(CO_3)_2]$ •$2H_2O$. The behaviors of these product salts in water, ethanol, and aqueous acid were investigated. The kinetics of the title reaction was monitored by conventional spectrophotometry at 525 and 635 nm over the following concentration ranges: $[Co(III)]$ = (5.7-1 1.4) X 10-4 M, $[H+]$ = (0.15-9.52) X 10-9 M, $[HCO3-]$ = 0.14-0.865 M and $[py]$ = (1.2-29.8) X 10-2 M at 25 ^{o}C and ionic strength 1.0 M ($NaHCO_3$, $NaCl0_4$). The rate law was found to be pseudo first order as the green solution turns to a purple solution after adding certain molar concentrations of pyridine. Spectral scanning during the course of the reaction showed that the rate-determining steps involve the formation of the first cobalt(II1)-pyridine bond, followed by rapid addition of pyridine to form the bis(carbonato)bis(pyridine)cobaltate(III) product. Another aspect that was studied throughout this experiment was the decomposition of the cobalt complex in nitric acid. Another result that was observed was that the decomposition of the carbonate ligands forms CO_2. The rate of decomposition of the carbonate ligands was also found to be pseudo first order.

Introduction: Synthesizing various carbonato complexes of transition metal ions in several oxidation states and their kinetic studies used to be a daunting task in the 70's and 80's, but now because of the advancement of modern day technology, it makes it a lot easier to synthesize and study these complexes and their kinetics. Studies of the $K[Co(py)_2(CO_3)_2]$ •$2H_2O$ have been well established. The objective of this study was to synthesize Bis (Carbonato) Bis (pyridine) cobaltate(III) Complex. The cobalt complex was used to study the characterization of the complex using IR and UV Spectroscopy to see if the synthesis was successful. This cobalt complex was placed in an acidic medium, HNO_3, and the decomposition kinetics were observed and recorded. Moving forward, kinetic studies were continued by observing the kinetics of the formation of the same species in-situ with variable concentrations of pyridine by keeping constant bicarbonate concentration. All measurements were carried out in 1 M ionic solution.

Experimental section:

Instrumentation: Ultraviolet- Visible Spectra were recorded using Genesys 10S UV – VIS Spectrophotometer (Model 610S serial number 2L5P123002). This instrument was also used to take the spectral scans of the formation and decomposition of the cobalt complex.

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Preparation of $K[Co(py)_2(CO_3)_2] \cdot 2H_2O$: The preparation of this complex was done in the method proposed by Geoffrey Davies and Yen-Wan Hung.
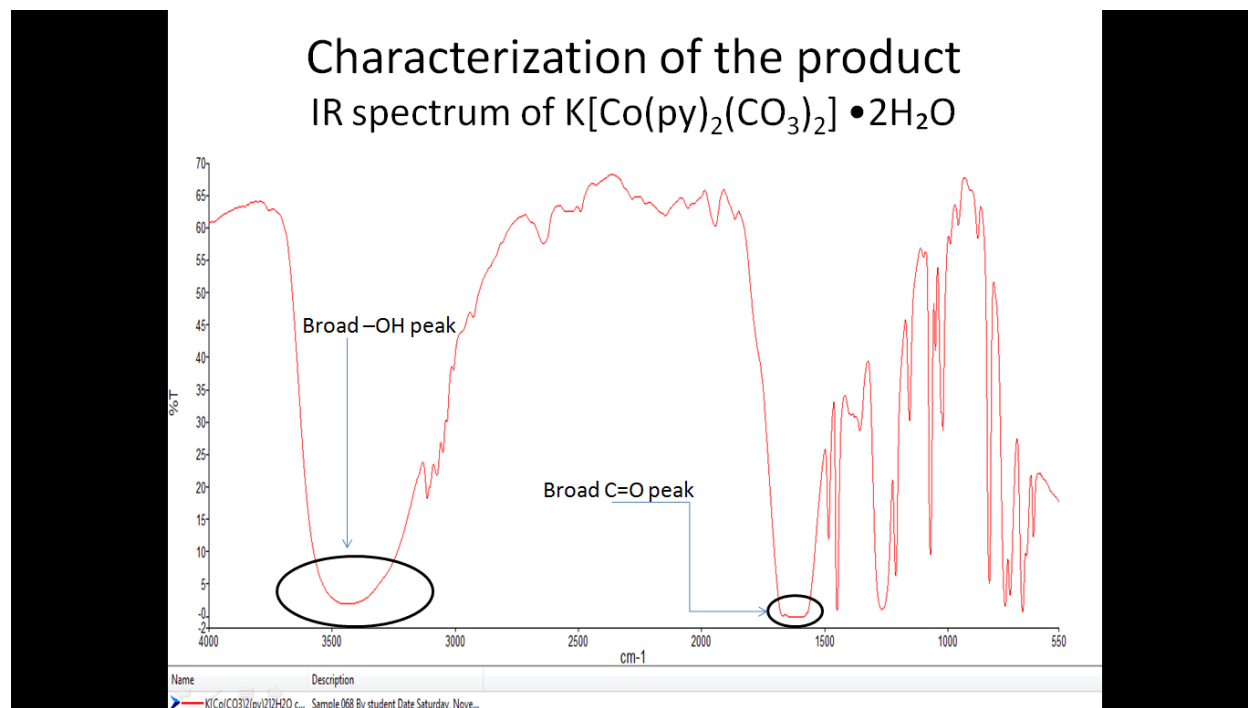
$Co(NO_3)_2 \cdot 6H_2O$ (1.21 g) and cold Hydrogen Peroxide (0.8mL) were measured out and transferred into a 50 mL beaker that was already placed in an ice bath and then stirred with a glass rod. Another ice bath was then set up with $KHCO_3$ (8.3g) and water (8.3ml) in another 50ml beaker with a magnetic stirrer. The red solution was then transferred by a Pasteur pipette to the $KHCO_3$ solution at a rate of 0.5 ml per minute. Upon addition of the red solution to the $KHCO_3$, the solution changed from clear to green. After adding all of the red solution, the green mixture was allowed to warm up to about 25 ^oC and then decanted into a 50 mL Erlenmeyer flask without any of the excess solid $KHCO_3$. Pyridine (0.3-3.3 ml) was then added to the flask and the reaction was allowed to proceed for 100 hours while stirred magnetically at 25 ^oC. The dark purple solution was poured into 300 ml of acetone and stirred for 30 min and then excess solvent was removed from the solid by decantation. The purple, wet solid was then washed with three 33 ml portions of anhydrous acetone and extracted with a small volume of ethanol (5ml). The solution was then poured into 166 ml of ice cold acetone and the solid was separated from the solvent by decantation and dried under vacuum over P2O5. (Yield of the product was determined to be 1.715g.)

Preparation of Crystals: of bis(carbonato)bis(pyridine)cobaltate(III) was attempted by the Bi-layer Diffusion crystal growth method using ethanol and acetone. 0.05 g of the complex was weighed out and dissolved in 3ml of ethanol. The solution was then poured into a test tube and clamped to a stand at a 45 degree angle. Next, roughly about 7 ml of acetone was then added to the tilted test tube in a drop wise fashion. The test tube was sealed with a cork and left undisturbed but monitored for a few days.

Reaction with Nitric acid: The bis(carbonato)bis(pyridine)cobaltate(III) solid product was dissolved in water and treated with 0.00239 mols of Nitric Acid.

Results and discussion: After completing the synthesis, the yield of the bis(carbonato)bis(pyridine)cobaltate(III) product was 1.397 g. The next step was to determine if the synthesis was successful by IR and Ultra Violet Visible Spectrometer scans.

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Characterization of the product
IR spectrum of $K[Co(py)_2(CO_3)_2] \bullet 2H_2O$

Broad –OH peak

Broad C=O peak

Name | Description
K[Co(CO3)2(py)2]2H2O c... Sample 068 By student Date Saturday, Nove...

Figure 1: IR spectra of $K[Co(py)_2(CO_3)_2] \bullet 2H_2O$

The spectrum in figure 1 shows an –OH peak from water in the compound around 3600 cm-1 and a carbonyl peak around the 1600-1700 range that proves that carbonate ligands exist in the complex.

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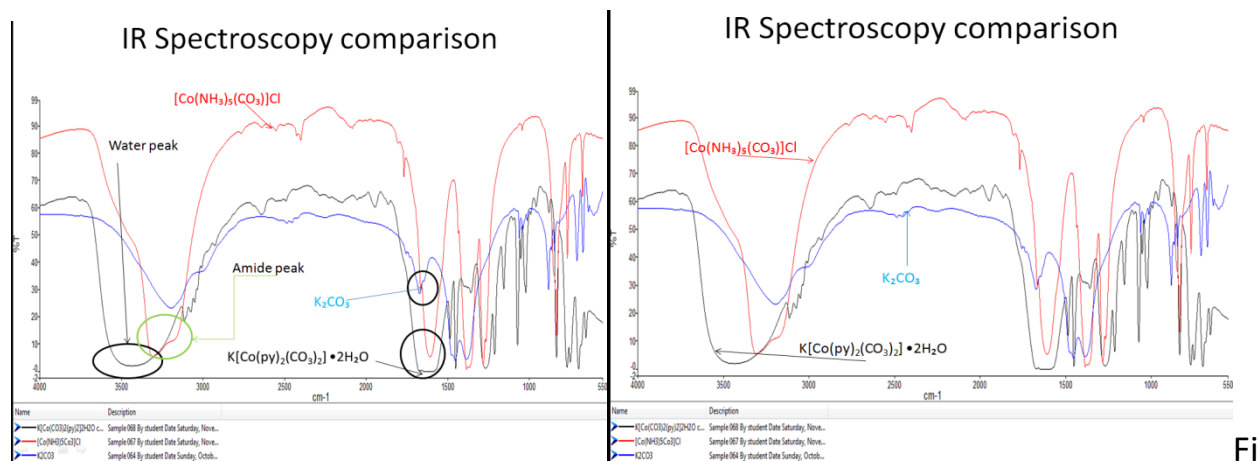
gures 2 and 3: IR Spectroscopy comparison

Next, the cobalt complex that was synthesized was compared to the K_2CO_3 and $[Co(NH_3)_5(CO_3)]Cl$ by taking the IR spectrum of them and overlaying them with $K[Co(py)_2(CO_3)_2] \cdot 2H_2O$ that was synthesized. As you can see, the carbonyl peak of the K_2CO_3 has lower energy compared to the carbonyl peaks of the coordinated metal complexes.

X-Ray Quality Crystal: Bi-Layer Diffusion Method

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After a week of monitoring has gone by no crystals have been formed in the test tube using the bi-layer diffusion method. This could've resulted from inadequate amounts of ethanol or acetone being added, an incorrect test tube size or the way it is was sealed. Another attempt shall be made with corrections. The next step was to study the Ultra-violet Visible spectra of the K[Co(py)$_2$(CO$_3$)$_2$] •2H$_2$O complex.
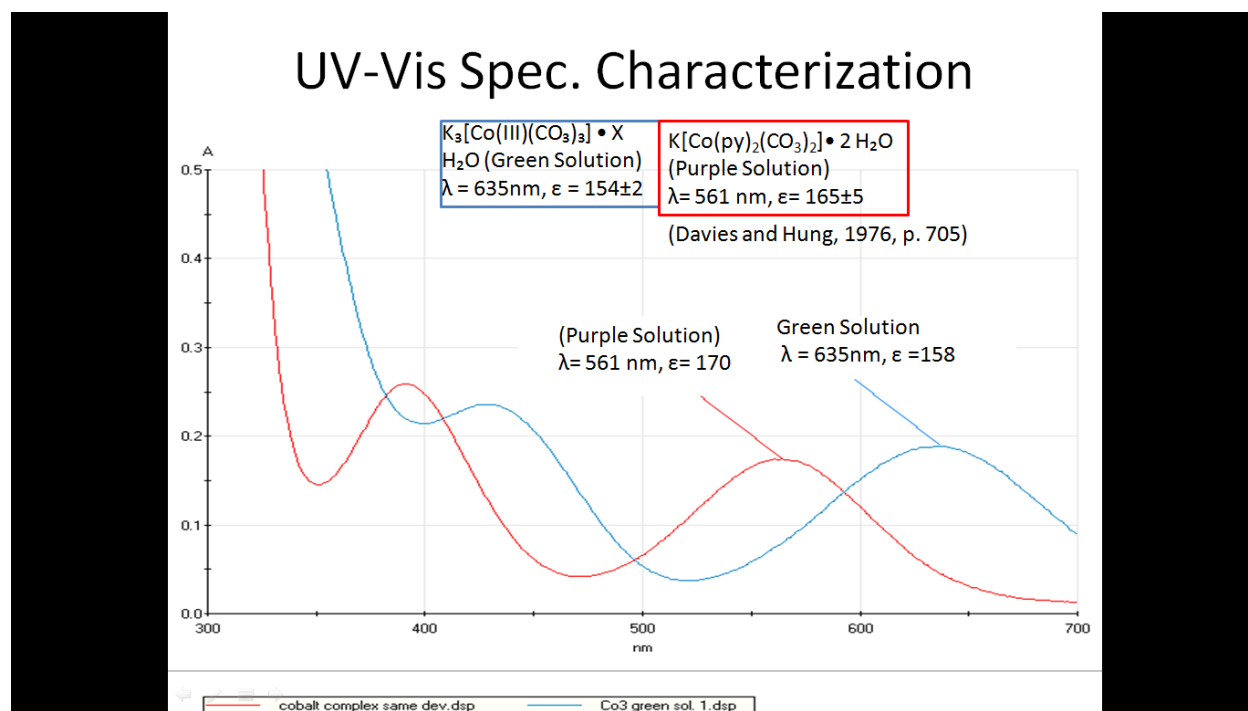
Figure 4 : Ultra-Violet Vis Spectrum of K[Co(py)$_2$(CO$_3$)$_2$] •2H$_2$O and K$_3$[Co(III)(CO$_3$)$_3$] • X H$_2$O

Figure 4 shows the UV – Vis spectra of both the K$_3$[Co(III)(CO$_3$)$_3$] • X H$_2$O (before pyridine) and the K[Co(py)$_2$(CO$_3$)$_2$] •2H$_2$O (after pyridine). Shown in this figure are the experimental values of lambda max of 561 nm for K[Co(py)$_2$(CO$_3$)$_2$] •2H$_2$O and an epsilon value of 170 as well as the lambda max of 635 nm for the K$_3$[Co(III)(CO$_3$)$_3$] • X H$_2$O an epsilon value of 158. These experimental values are comparable to the theoretical values obtained from the reference experiment. Following this, the study of the kinetics of the formation of the species using 1 molar ionic concentration and varying the concentrations of pyridine was conducted.

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Formation of Cobalt Complex
0.3M pyridine
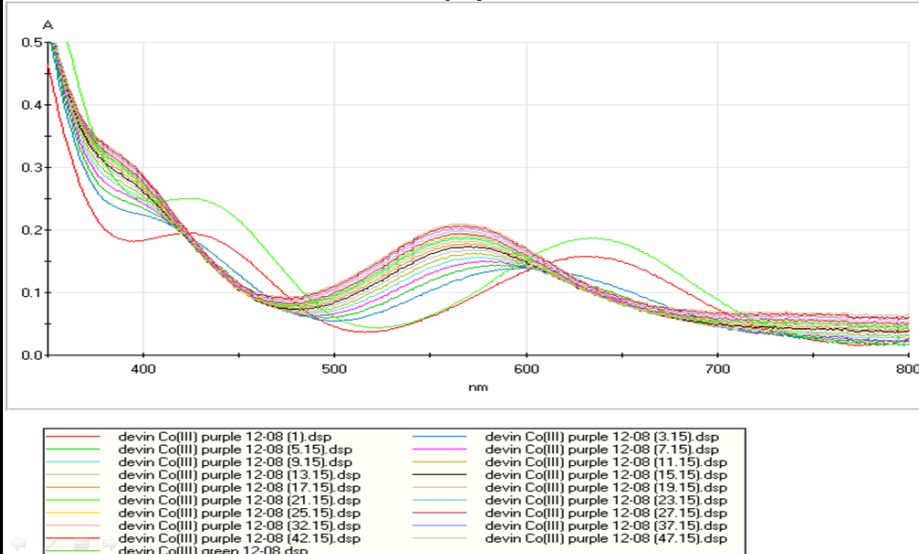
Title: Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato
Complexes: Rate of Decarboxylation of the Bis(carbonato)bis
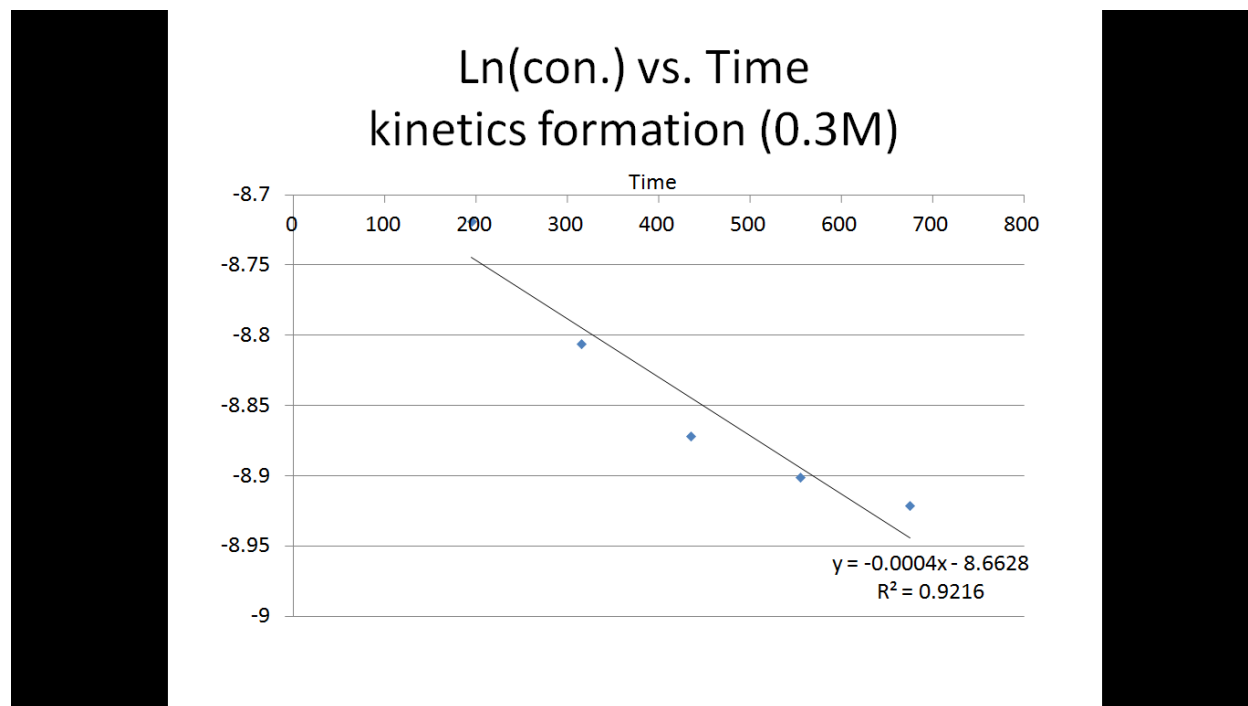(pyridine)cobaltate(III) complex ion in Aqueous Pyridine Buffer Solutions
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Figure 5: UV-Vis spectra of the formation of Cobalt Complex using 0.3 M pyridine and a graph of ln(con.) vs time.

Shown in figure 5 is the spectra of the formation of $K[Co(py)_2(CO_3)_2] \cdot 2H_2O$ as it goes from a green color to the purple color after adding 0.3 M pyridine over time. Using the 0.3 M pyridine you cannot see the isosbestic points clearly, and as shown in the graph the slope of the plotted points is not straight showing that the rate of formation isn't pseudo first order.
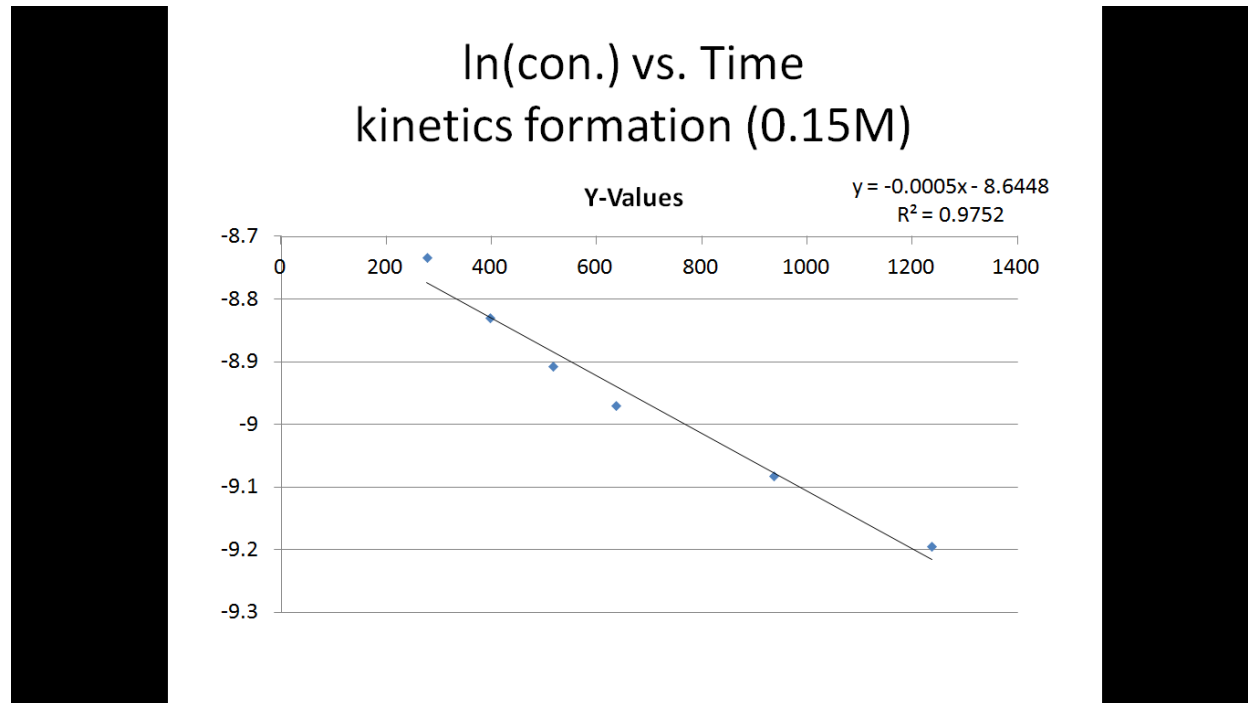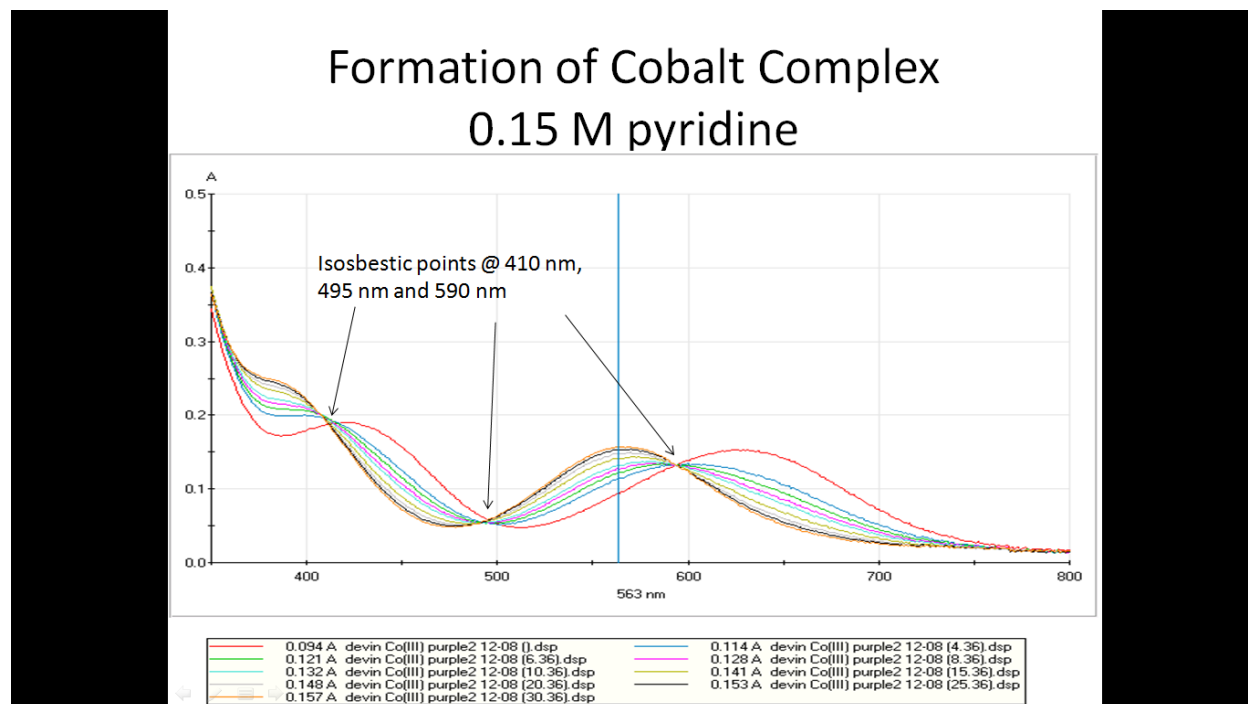
Figure 6: UV-Vis spectra of the formation of Cobalt Complex using 0.15 M pyridine and the graph of ln(con.) vs time.
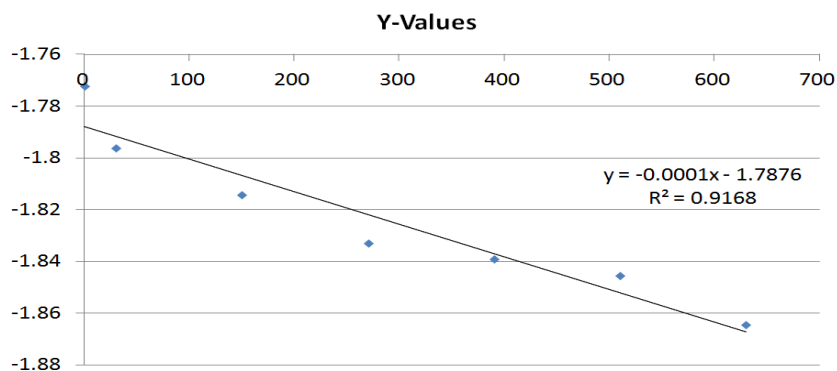
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After lowering the concentration of pyridine by half, the isosbestic points are clearly visible at 410, 495 and 590 nm and after plotting a graph of ln(con.) vs time, the plotted points seem to be straightening out and showing the rate of formation going towards pseudo first order.

UV spectrum of Decomposition of $K[Co(py)_2(CO_3)_2] \bullet 2H_2O$ using HNO_3
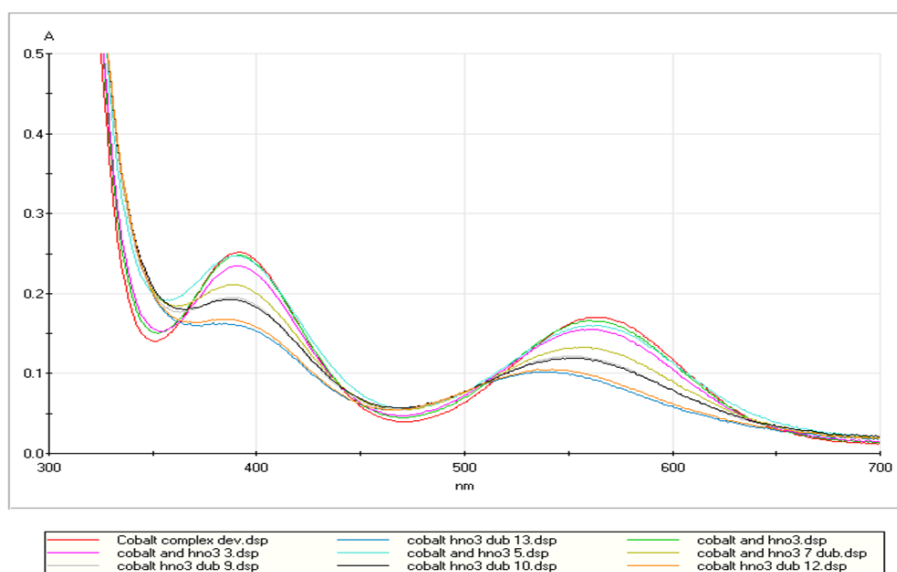
ln(Absorbance) vs. Time of Decomposition

y = -0.0001x - 1.7876
R² = 0.9168

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Following this, the study of decomposition of the carbonate ligands in the cobalt complex after the addition of nitric acid was studied and recorded. After adding 0.00239 mols of HNO3 over the course of 16 min, recording a scan every 2 minutes, the depletion of the wavelength was shown. Using the absorbance values of the cobalt complex at 635 nm and plotting a graph of the ln(absorbance) vs. time, it is shown that it isn't first order although the literature proves to be first order for the decomposition of the same cobalt complex using Perchloric acid.

Conclusion: In conclusion, 0.3M pyridine or stronger concentrations seem to change the order of the rate. By lowering the concentration by half it shows that the rate is pseudo first order, so concentrations even lower than 0.15 M may bring the rate formation closer, if not make the rate pseudo first order. One possible reason for the different kinetics observed is the use of HNO_3 vs. $HClO_4$ since the rate of decomposition using Perchloric acid is pseudo first order and the same results weren't produce by Nitric acid.

Reference

1. Hyde, K., Hyde, E., Moryl, J., Baltus, R., & Harris, G. (1979). Kinetics and mechanism of aquation and formation reactions of carbonato complexes. 19. Rate of decarboxylation of the bis(carbonato)bis(pyridine)cobaltate(III) complex ion in aqueous pyridine buffer solutions. *Inorganic Chemistry,* 1603-1607.
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Acknowledgements

- Dr. Phalguni Ghosh

- Dr. Steven Rowley

- Dr. Parag Muley

- Dr. Brian Levy

- Dean David Edwards

- Chemistry Lab Staff

- Peer Students(Tram Tran, Anh Ngo, Mohammed Vayani)

- Bristol-Meyers Squibb for financial support