

Title: Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes: Rate of Decarboxylation of the Bis(carbonato)bis(pyridine)cobalt(III) Complex Ion I Aqueous Pyridine Buffer Solution

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Abstract: The synthesis of the metal coordination was prepared by dissolving $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ in aqueous sodium bicarbonate. The reaction of these green solutions with excess pyridine was found to produce only $\text{cis-Co}(\text{CO}_3)_2(\text{py})_2(\text{aq})$, which was isolated as a pale blue, moisture-sensitive hydrate $\text{K}[\text{Co}(\text{CO}_3)_2(\text{py})_2] \cdot 0.5\text{H}_2\text{O}$ and as the purple crystalline salt $\text{K}[\text{Co}(\text{CO}_3)_2(\text{py})_2] \cdot 2\text{H}_2\text{O}$. The behavior of these product salts in water, ethanol, and aqueous acid was investigated. The kinetics of the title reaction was monitored by conventional spectrophotometry at 525 and 635 nm over the following concentration ranges: $[\text{CoIII}] = (5.7-11.4) \times 10^{-4} \text{ M}$, $[\text{H}^+] = (0.15-9.52) \times 10^{-9} \text{ M}$, $[\text{HCO}_3^-] = 0.14-0.865 \text{ M}$, and $[\text{py}] = (1.2-29.8) \times 10^{-2} \text{ M}$ at 25 °C and ionic strength 1.0 M (NaHCO_3 , NaClO_4). The rate law was found to be pseudo first order as the green solution turns to a purple solution after adding certain molar concentration of pyridine. Spectral scanning during the course of the reaction showed that the rate-determining steps involve the formation of the first cobalt(III) 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.

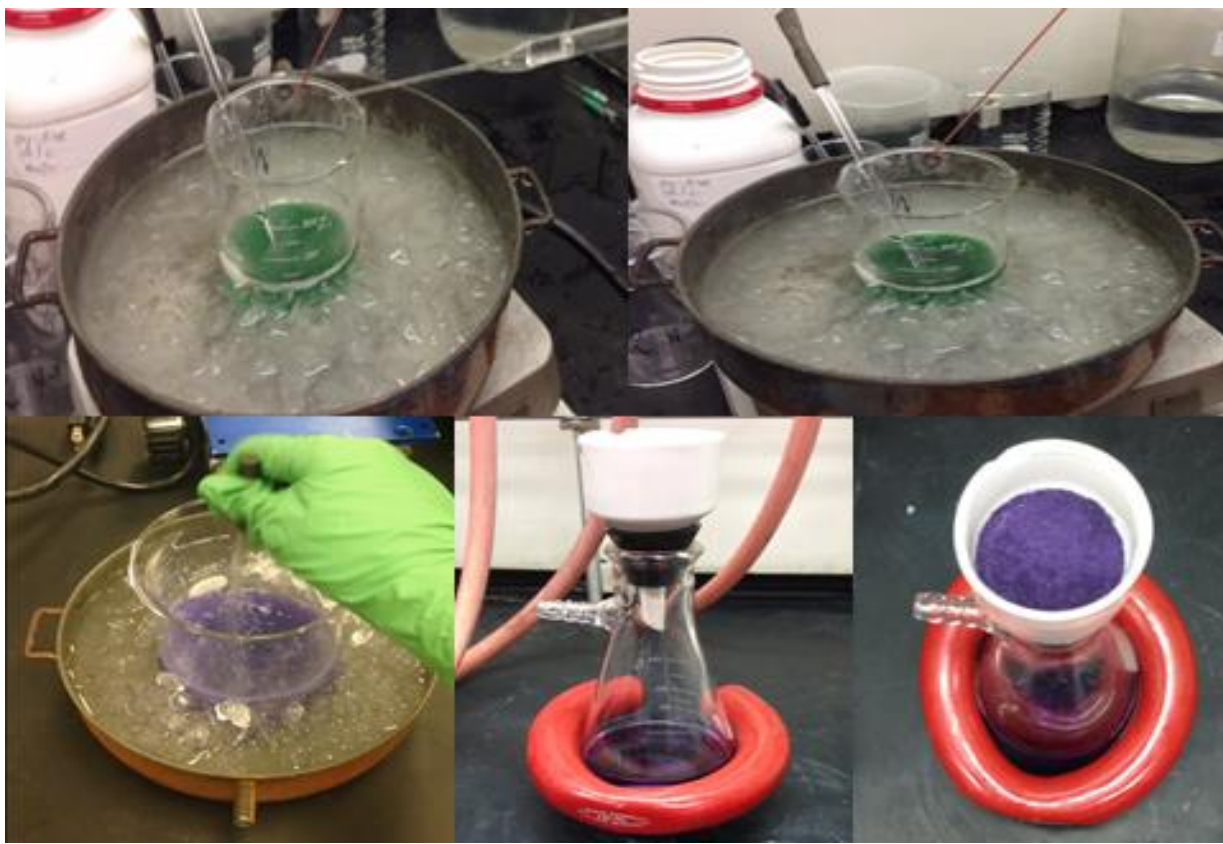
Introduction: Synthesizing various carbonato complexes of transition metal ions several oxidation states and their kinetic studies used to be a daunting task in the 70's and 80's, but now because of modern day technology has advanced, it makes it a lot easier to synthesize and study these complexes and their kinetics. Studies of the $\text{K}[\text{Co}(\text{py})_2(\text{CO}_3)_2] \cdot 2\text{H}_2\text{O}$ have been well established. The objectives of this study was to synthesis Bis(Carbonato) Bis(pyridine)cobaltate(III) Complex. The cobalt complex was used to study the characterization of the complex using UV Spectroscopy to see 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. The kinetics of decomposition were continued by first maintain the temperature and changing pH and then Bu maintain pH and varying the temperature.

Experimental Section:

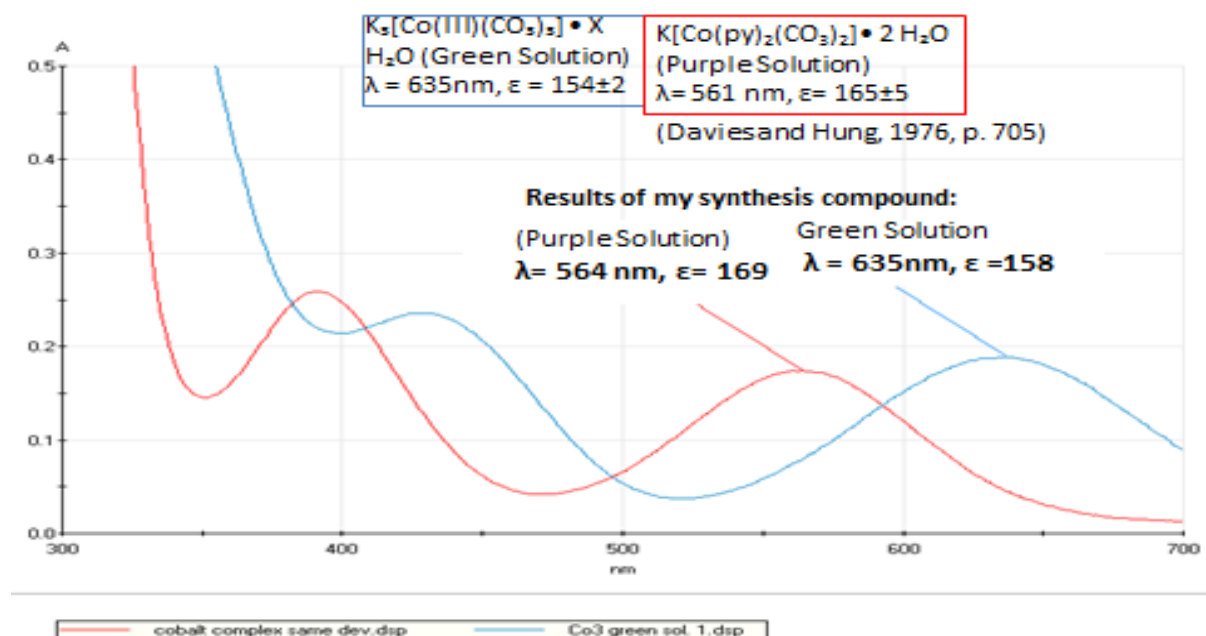
Instrumentation: Ultraviolet-Visible Scanning Spectrophotometer and Ultraviolet-Visible fixed wavelength Spectrophotometer.

Preparation: Hydrated potassium cis-bis(carbonato) bis(pyridine)cobaltate(III) salts $\text{K}[\text{Co}(\text{CO}_3)_2(\text{py})_2] \cdot x\text{H}_2\text{O}$ ($x = 0.5$ or 2), were synthesized as follows. An ice-cold solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (7.3 g) in 10 ml of water was mixed with ice-cold hydrogen peroxide (30% w/v, 5 ml) and the mixture was then added at a rate of 0.5 ml min⁻¹ to a constantly stirred, ice-cold slurry of KHCO_3 (50g) in 50 ml of water. After addition of all of the cobalt-(1L)-peroxide mixture, the resulting green solution was allowed to warm to 25 °C and the supernatant were decanted from excess solid KHCO_3 into a stoppered Erlenmeyer flask. Pyridine (20 ml) was then added and reaction was allowed to proceed for 100 h at 25 °C, at which time no further spectral changes were evident. The dark purple product mixture was poured into 2 L Of ice-

cold acetone and stirred for 30 min; excess solvent was then removed from the solid by decantation. The wet, purple solid was then washed by decantation with three 200-ml portions of anhydrous acetone and extracted with a minimum volume of ice-cold ethanol (30 ml) and the solution was quickly poured into 1 L of ice-cold, anhydrous acetone. The pale blue, highly deliquescent 1L precipitate was then washed by decantation with two 200-ml portions of anhydrous acetone and dried under vacuum. Final product obtained after recrystallization of the crude product from ethanol and acetone. The yield of product was determined to be 0.1731g.



UV-Vis Spec. Characterization




Kinetics of Formation: The baseline solution was prepared by adding 1M $NaHCO_3$, 2M $NaNO_3$, H_2O , 1M HNO_3 . After that, the 1M solution of cobalt nitrate hexahydrate was added directly into the cuvette and the spectrum was determined. Then 10M of pyridine was again directly added into the same cuvette in order to perform the kinetics of formation. The plot of natural log ($\ln [CR]$) of the concentration of reactant versus time (t) gave k_{obsd} .

$$CR = (A_{total, 640} - \epsilon_{P, 640} * C_{R, 0}) / (\epsilon_{R, 640} - \epsilon_{P, 640})$$

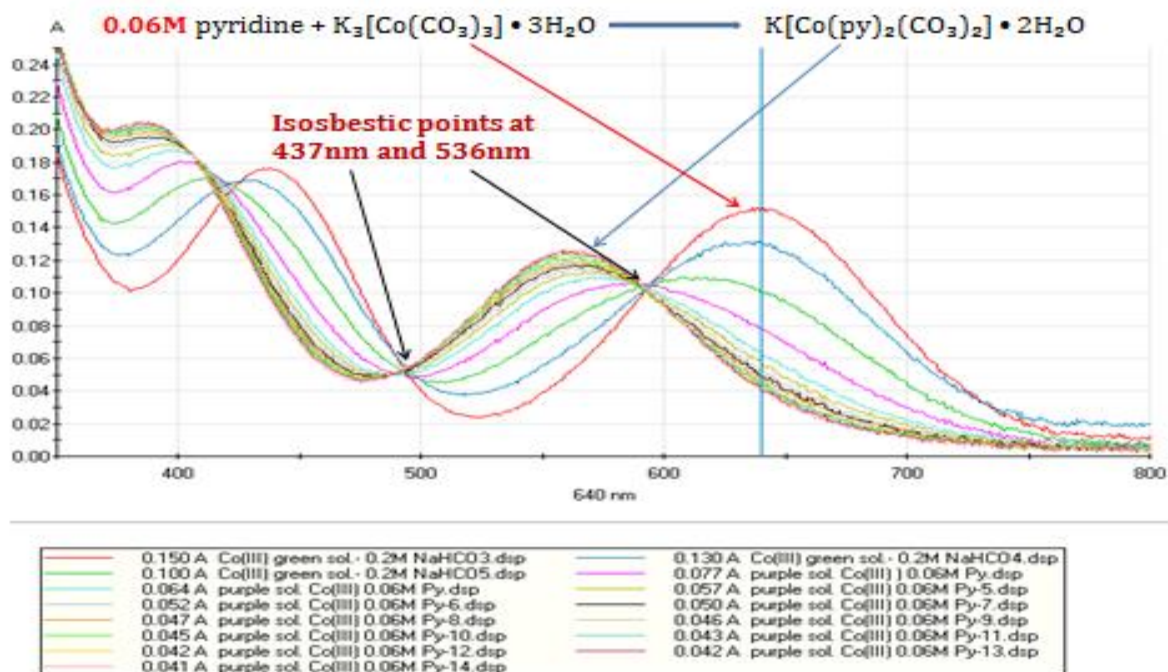


$K_3Co(CO_3)_3$

Pyridine




$KCo(CO_3)_2 py_2$



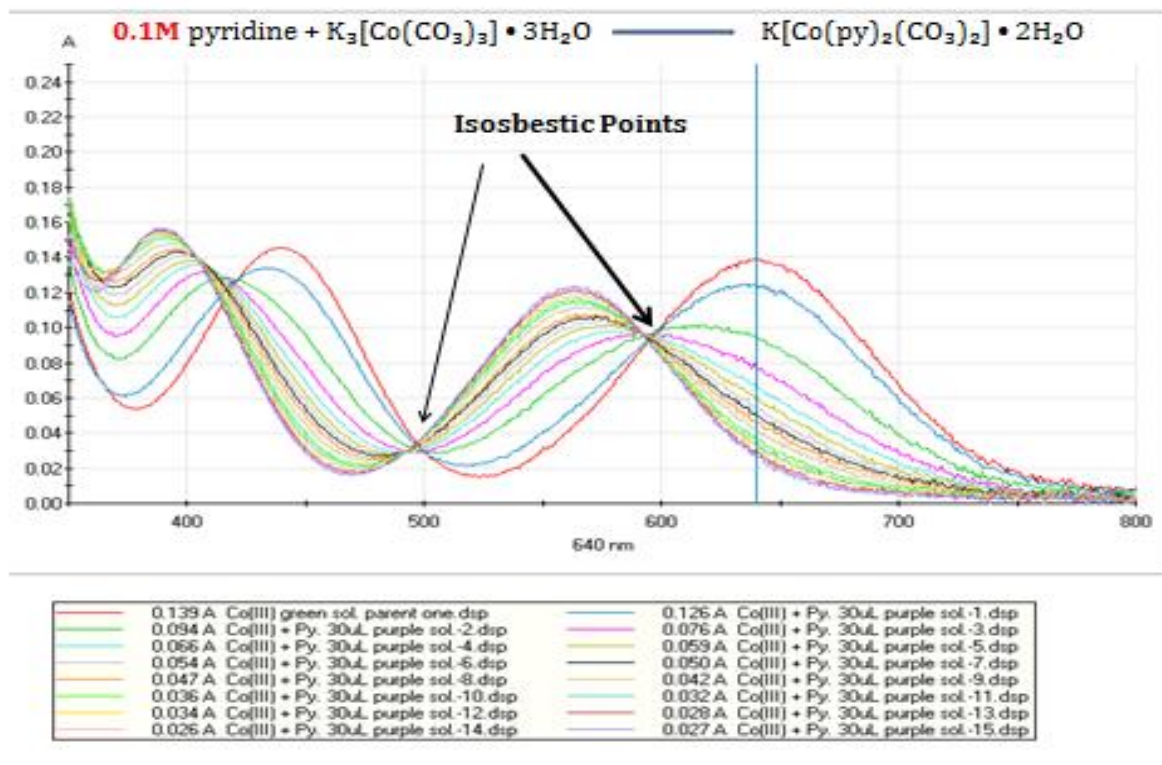
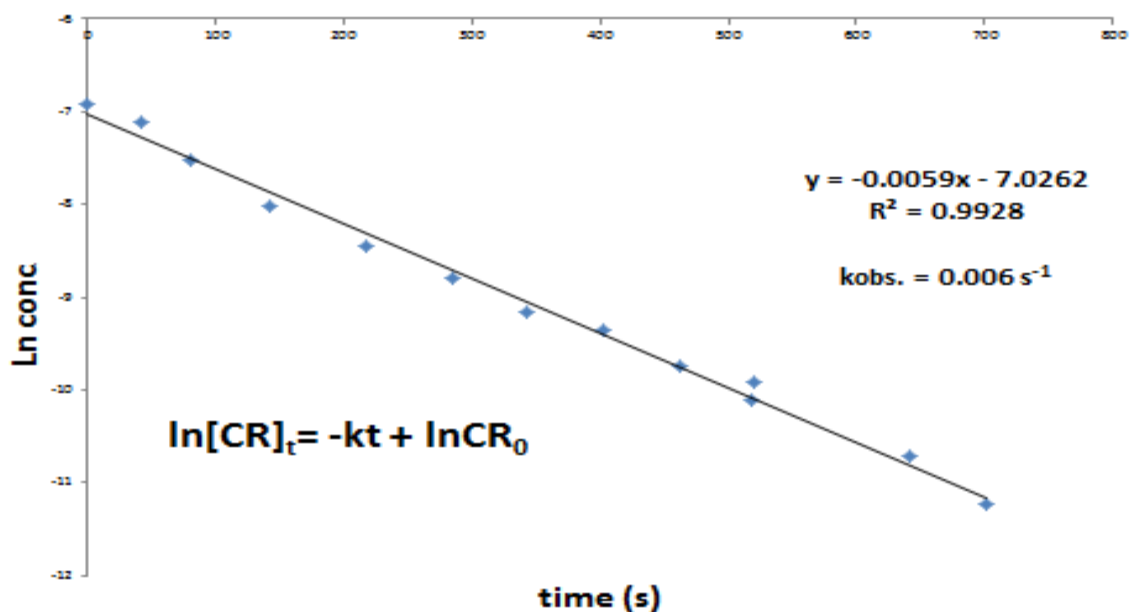
Kinetic of Formation with 0.06M pyridine

absorbance	CR	Time (s)	ln(CR)
0.15	0.001	0	-6.90776
0.13	0.000817	42	-7.10954
0.1	0.000543	81	-7.51809
0.077	0.000333	142	-8.00728
0.064	0.000214	218	-8.44835
0.057	0.00015	285	-8.8029
0.052	0.000105	342	-9.16523
0.05	8.63E-05	403	-9.35721
0.047	5.89E-05	462	-9.73914
0.046	4.98E-05	521	-9.90761
0.045	4.07E-05	518	-10.1103
0.043	2.24E-05	641	-10.7071
0.042	1.32E-05	701	-11.2317
ER 640	150		
EP 640	40.55		

The Rate of formation of compound follows the first order rate law

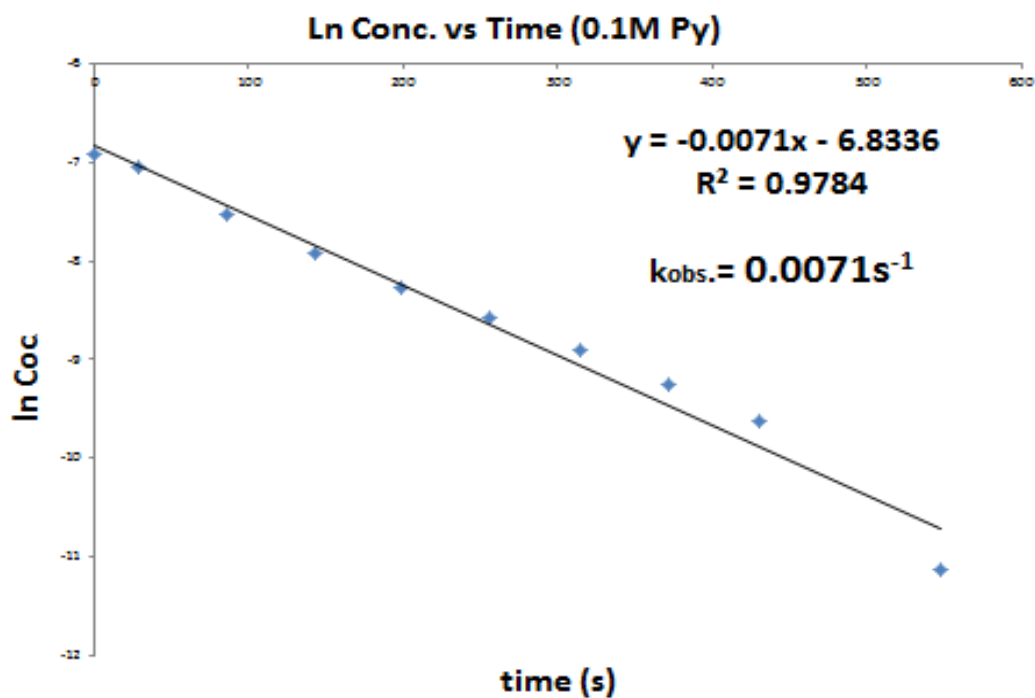
$$\text{Rate} = k[Co(CO_3)_3^{3-}]$$

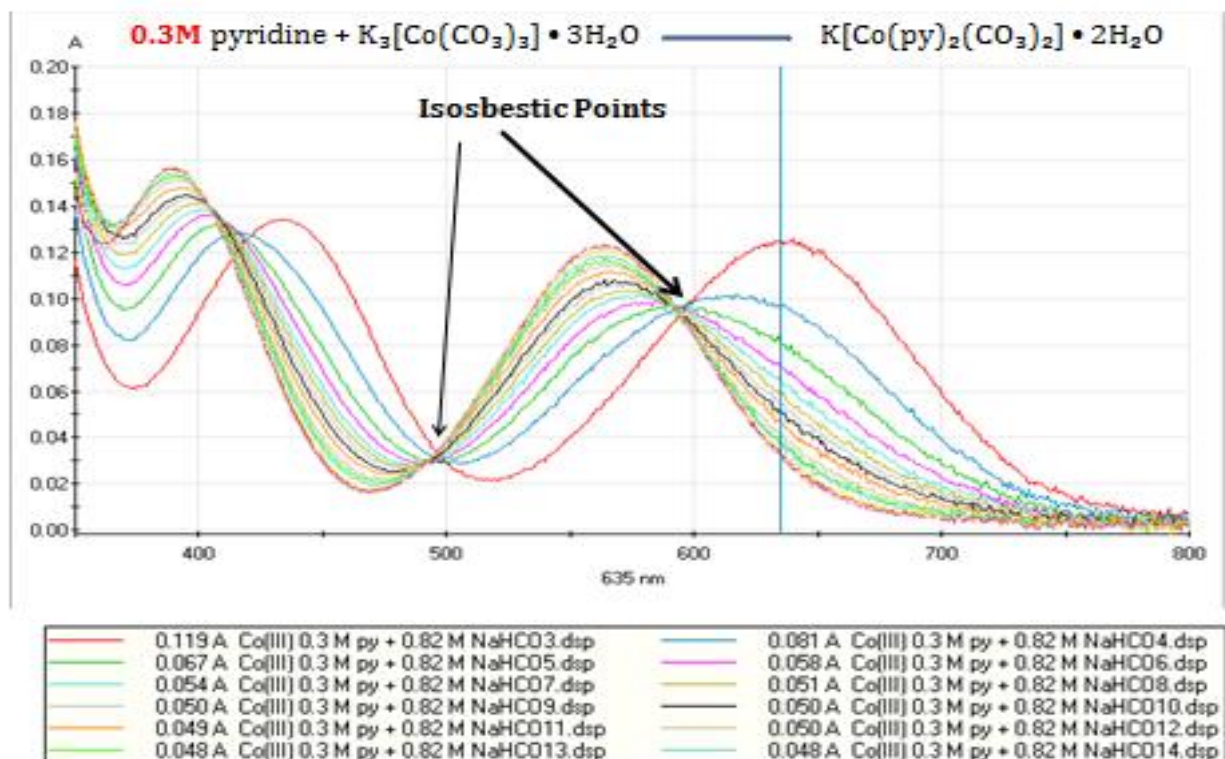
Ln conc. vs time (0.06M Py)



Kinetic of Formation with 0.1M Pyridine

absorbance	CR		Time (s)	Ln CR
0.139	0.001		0	-6.90776
0.126	0.000868		29	-7.04937
0.094	0.000543		86	-7.51856
0.076	0.00036		143	-7.92918
0.066	0.000259		199	-8.26059
0.059	0.000187		256	-8.58224
0.054	0.000137		314	-8.89832
0.05	9.6E-05		371	-9.25129
0.047	6.55E-05		430	-9.63322
0.042	1.47E-05		548	-11.1257
ER	139			
EP	40.55			

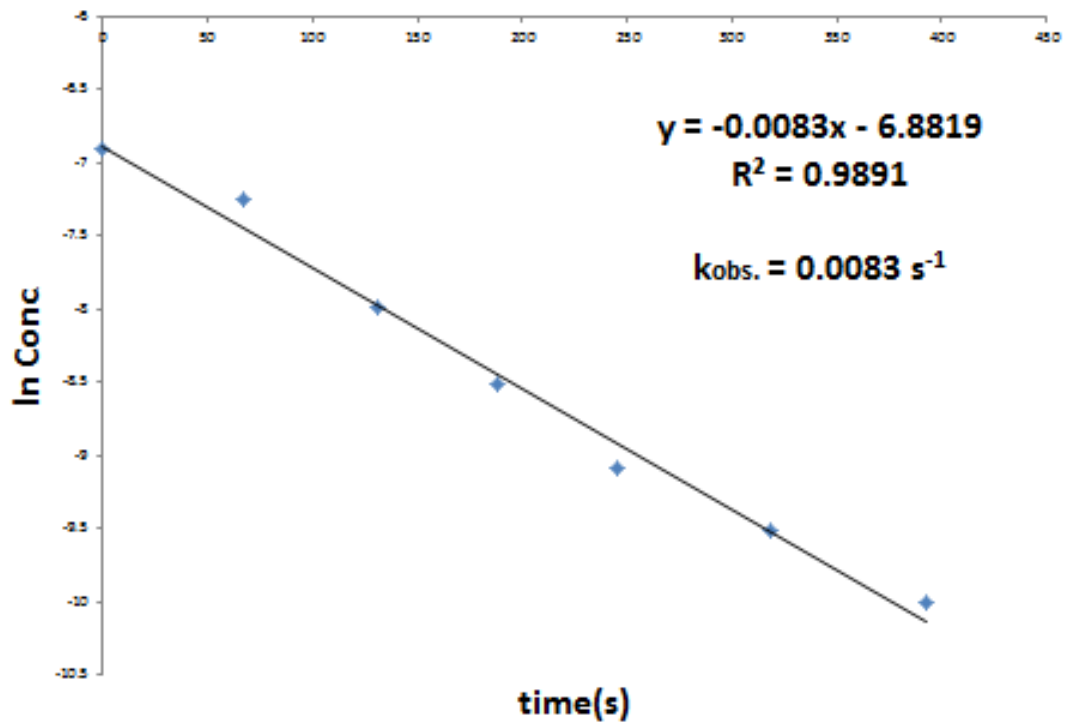




Kinetic of Formation with 0.3M pyridine

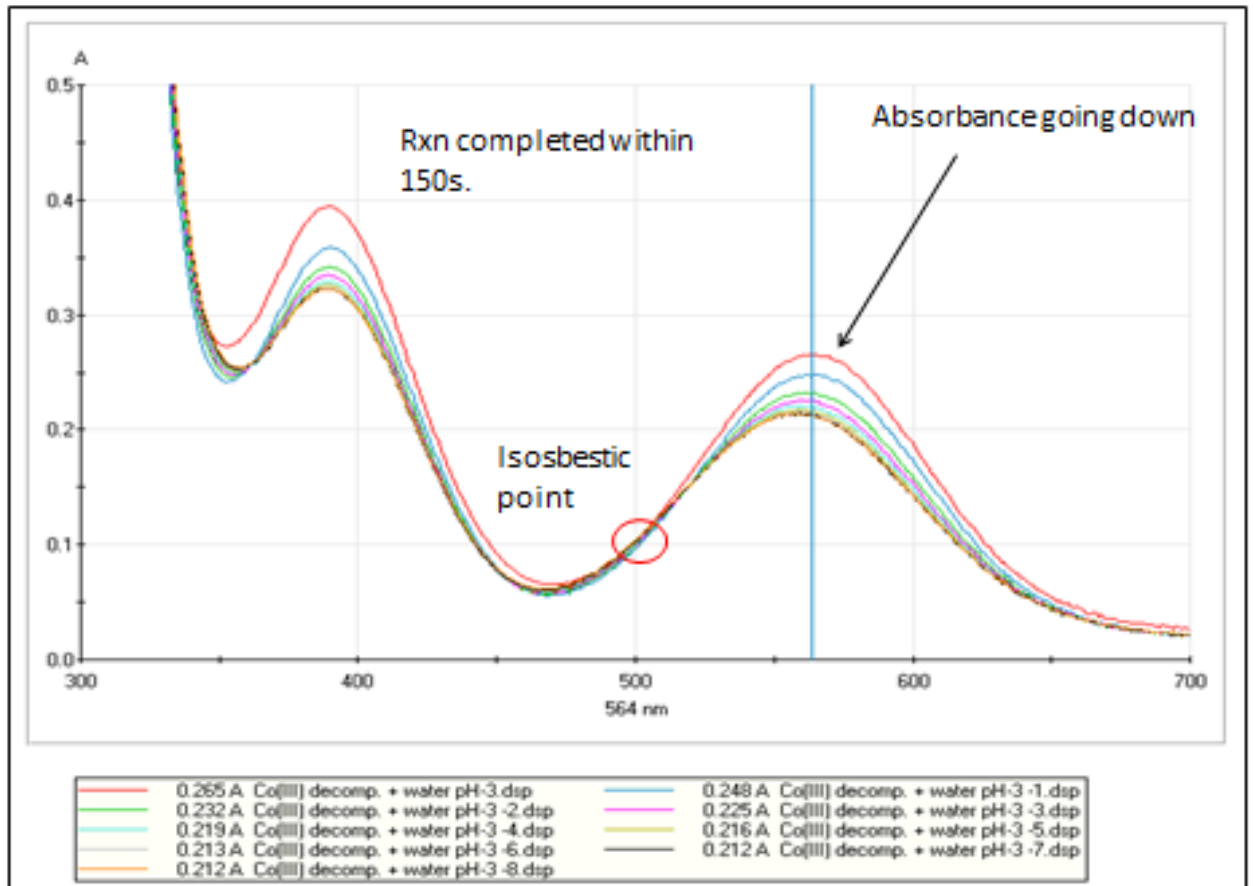
Absorbance	CR	time(s)	Ln CR
0.149	0.001	0	-6.90776
0.119	0.000708	67	-7.25363
0.081	0.000337	131	-7.99474
0.067	0.000201	188	-8.5133
0.058	0.000113	245	-9.08759
0.054	7.41E-05	319	-9.51044
0.051	4.48E-05	393	-10.0125
0.05	3.51E-05	534	-10.2577
0.049	2.53E-05	604	-10.5831
0.048	1.56E-05	824	-11.0686
ER 635	149		
EP 635	46.6		

In Conc. vs Time (0.3M Py)



Kinetics of Decomposition: The baseline solution of this reaction was just simple De-ionized water. The parent spectrum was determined by the solution of solid purple compound and water. Later the kinetics of decomposition was done by adding certain amount of 2M of nitric acid in the purple solution at 25°C.

UV spectrum of decomposition of $\text{Co(III)(py)}_2(\text{CO}_3)_2$ at **pH-3.17** at 25°C



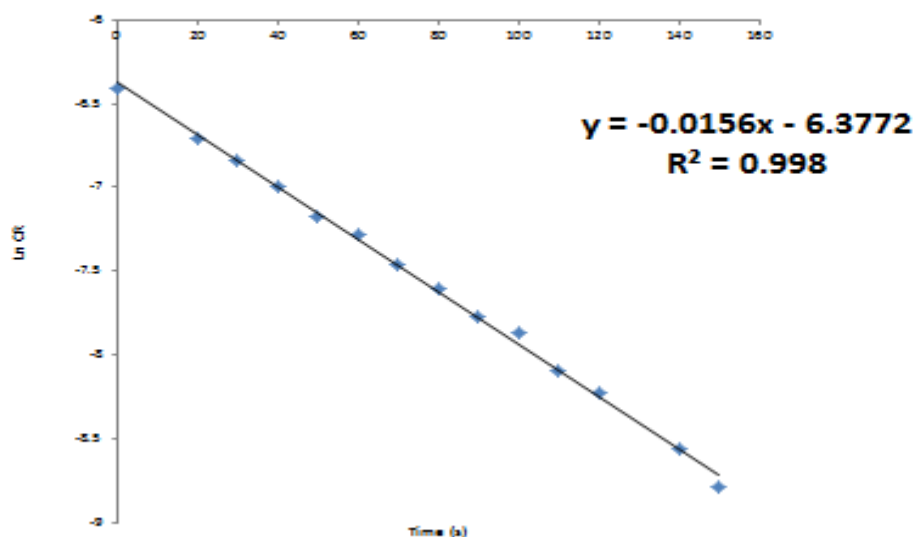
Kinetics of decomposition at pH-3.17 at 25° C

Absorbance 564nm	CR 564nm	Time (s)	Ln CR
0.241	0.0016437	0	-6.411
0.23	0.0012232	20	-6.706
0.226	0.0010703	30	-6.84
0.222	0.0009174	40	-6.994
0.218	0.0007645	50	-7.176
0.216	0.0006881	60	-7.282
0.213	0.0005734	70	-7.464
0.211	0.0004969	80	-7.607
0.209	0.0004205	90	-7.774
0.208	0.0003823	100	-7.869
0.206	0.0003058	110	-8.093
0.205	0.0002676	120	-8.226
0.203	0.0001911	140	-8.562
0.202	0.0001529	150	-8.786
EP 564nm	120.445		
ER 564nm	146.60259		
CrO	1.6439E-03		

The Rate of Decomposition of compound follows the first order rate law

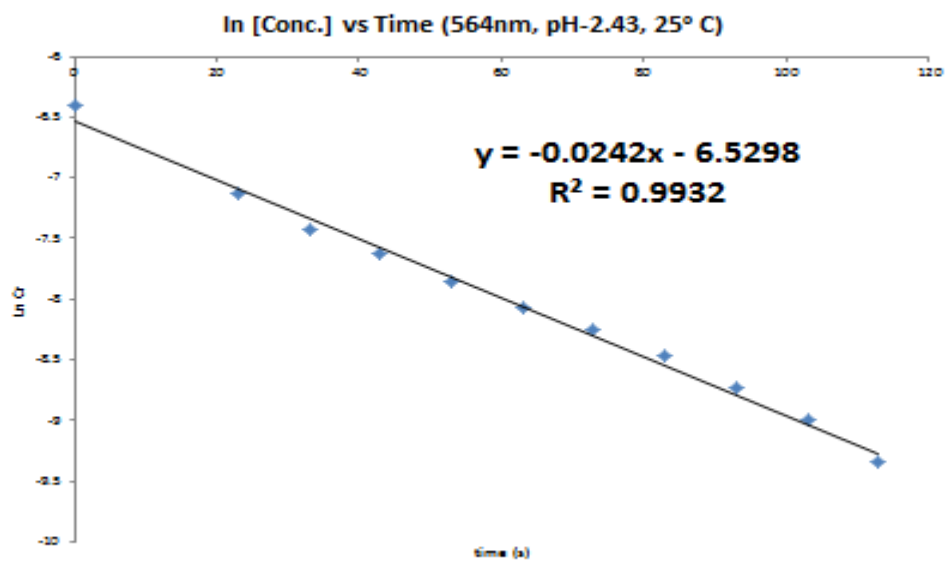
$$\text{Rate} = k_{\text{obs}} [\text{complex}]$$

ln [conc.] vs Time (564nm, pH=3.17, 25° C)



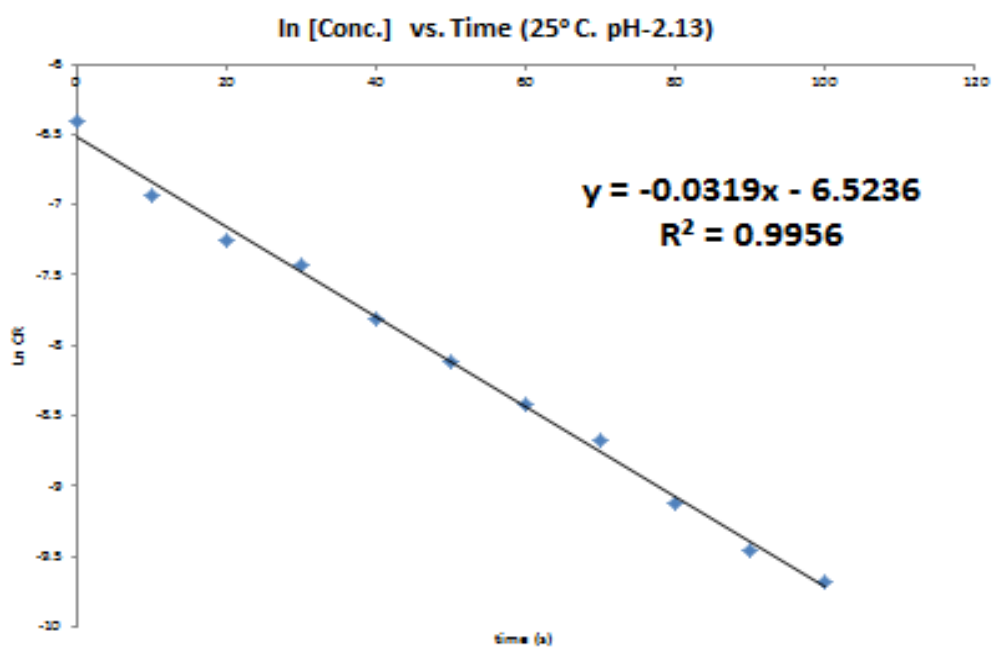
Kinetics of decomposition at pH-2.43 at 25° C

Absorbance 564nm	CR 564nm		Time (s)	Ln CR 564nm
0.244	0.0016439		0	-6.41068
0.176	0.000797		23	-7.1346
0.16	0.0005978		33	-7.42229
0.151	0.0004857		43	-7.62993
0.143	0.0003861		53	-7.85951
0.137	0.0003113		63	-8.07462
0.133	0.0002615		73	-8.24898
0.129	0.0002117		83	-8.46029
0.125	0.0001619		93	-8.72857
0.122	0.0001245		103	-8.99095
0.119	8.717E-05		113	-9.34764
Er 564nm	148.427			
Ep 564nm	68.131			
Cr0	1.6439E-03			



Kinetics of decomposition at pH-2.13 at 25° C

Absorbance 450nm	CR 564nm		time(s)	Ln CR
0.253	0.0016439		0	-6.41066
0.21	0.0009707		10	-6.93748
0.193	0.0007046		20	-7.25794
0.186	0.000595		30	-7.42701
0.174	0.0004071		40	-7.80649
0.167	0.0002975		50	-8.12012
0.162	0.0002192		60	-8.42548
0.159	0.0001722		70	-8.66661
0.155	0.0001096		80	-9.11852
0.153	7.83E-05		90	-9.4549
0.152	6.265E-05		100	-9.67797
EP 564nm	90.0298			
ER 564nm	153.902			
CrO	1.6439E-03			

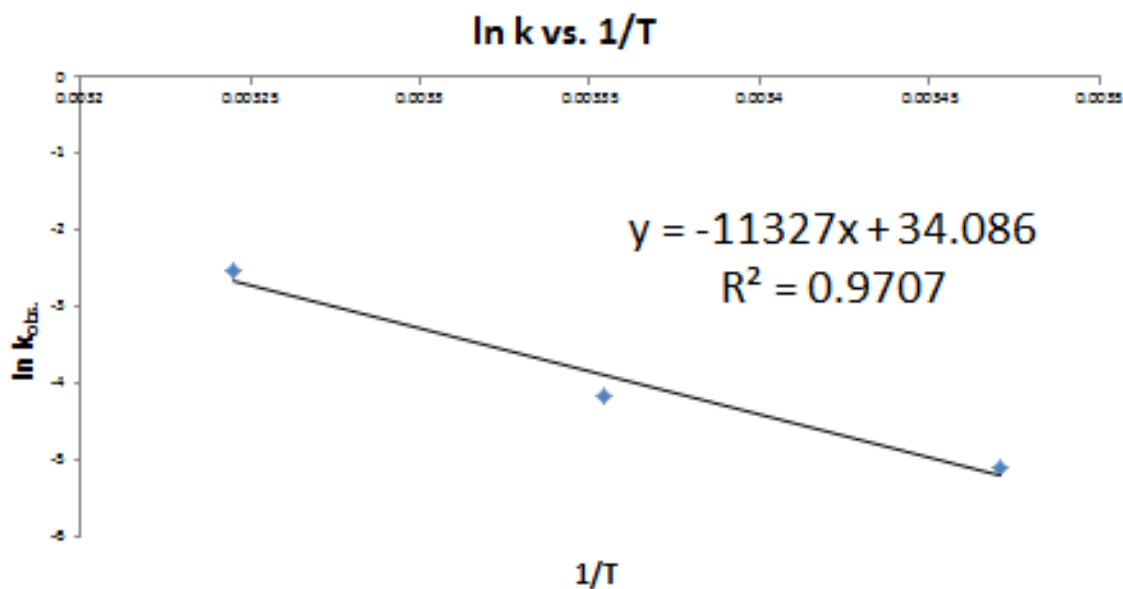


Determination of rate constants (k_x and k_y): k_x is the acid independence of the rate constant for decomposition process and k_y is the acid dependence of the rate constant for decomposition process. k_y was determined by plotting the $[H_3O^+]$ versus the k_{obsd} . The value of k_y was substituted in the equation below in order to calculate the value of k_x

$$k_{obsd} = k_x + k_y[H_3O^+]$$

The value of k_y is $2.1426 \text{ M}^{-1} \text{ s}^{-1}$ and the average value for k_x is 4.79 s^{-1}

Determination of the Arrhenius parameters: The baseline solution of this reaction was just simple De-ionized water. The parent spectrum was determined by the solution of solid purple compound and water. Later the kinetics was done at different by adding 2M of nitric acid in the purple solution by maintain the pH 3.17. Arrhenius parameters were determined by plotting natural log of k and $1/\text{temperature}$.



1/T	0.00347	0.003354	0.003245
ln k_{obs}	-5.09947	-4.16048	-2.53957

Activation energy (E_a) = 94.17 kJ/mole

$A = 6.359 \times 10^{14} \text{ s}^{-1}$

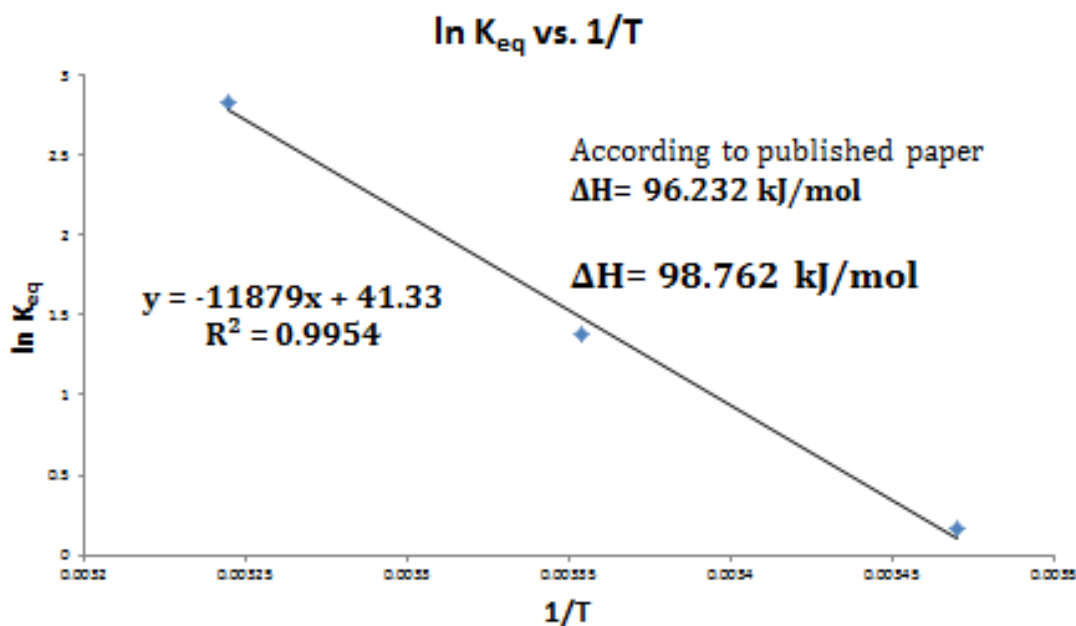
Determination of ΔH : ΔH is change in enthalpy. The graph of $\ln K_{eq}$ vs. $1/T$ gives the value of ΔH . The equation below was used in order to determine the change in enthalpy.

$$\Delta G^{\circ} = - RT \ln K_{eq}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$- RT \ln K_{eq} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\ln K_{eq} = - \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$



$1/T$	0.00347	0.003354	0.003245
$\ln K_{eq}$	0.159166	1.38112	2.835291

Results and Discussion: The synthesis of this coordination compound was successful. From the Kinetics of formation, the Observed rate constant (k_{obs}) increased with the concentration of pyridine. Rate of formation of the product follows pseudo first order rate with respect to the starting materials. From the kinetics of decomposition, at constant temperature (25° C), the rate constant (k_{obs}) increases as the pH goes down indicating this behavior is adequately described by a simple first-order hydrogen ion concentration. Observed rate constant (k_{obs}) increased with the rise in temperature as expected. ΔH calculated from my experiment matches with the literature value.

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References:

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