

Title: Studying the Complex Kinetics of Tris (1,10-Phenanthroline) and Iron (II) With Commercial Bleach

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Abstract: The synthesis of the Iron Complex was done in-situ with 3.1 equivalents of 1,10-Phenanthroline and 1 equivalent of Iron (II) Ammonium Sulfate. This gave a stock solution of 1×10^{-3} M. Afterwards a titration of commercial bleach (Clorox) was performed, taking reference from General Chemistry Book, 10th Edition by Raymond Chang, pages 156-159. Using the reference to find the concentration of NaOCl (1.33 M), which will be the substitute for HOCl that was used in the original lab report. Followed by creating three different Sodium Borate Buffers of pHs 8.78, 8.38, and 5, along with varying concentrations of NaOCl, and temperature. Monitoring this reaction using the UV-Visible Spectrophotometer at 510 nm, the rate of reaction will be observed based off the concentration as well as pH. For pHs 8.78 and 8.38, the concentrations used were 4.33×10^{-3} M, 1.33×10^{-2} M and 2.66×10^{-2} M, while for pH 5 the concentrations were given even smaller concentrations due to how fast the reaction occurred. When comparing my results to the literature values, it was found that the reactions with bleach occurred much faster in comparison. It is later concluded that the bleach likely Cl_2 gas, which is a strong oxidizing agent, which would explain the differences in results.

Introduction: In imitation to "The reaction of Tris (1,10-Phenanthroline) Iron(II) Ion with Chlorine(I) Species" by Martin G. Ondrus and Gilbert Gordon, published in 1971, this lab is recreating their procedure, but rather than using HOCl as was used in the original lab report, bleach will be used instead to gain the Cl^+ Ion. The following objective is to study the complex compound $\text{Fe}(\text{Phen})_3^{2+}$ and its oxidation in commercial bleach (Clorox), which contains 1.33 M of NaOCl. This is done because the laboratory does not hold any HOCl and or any NaOCl. The authors had performed these procedures under pseudo-first order conditions in which Cl^+ is given in excess, and have concluded there to be two different pathways during the reaction, the first to occur being dissociation, the other to be a one-electron oxidation. When creating their own formula to calculate the k_{obsd} values, values k_0 represented the rate of dissociation while k_1 and k_2 represented rates independent of dissociation. Then to study these reactions, they are performed under three different pHs (8.78, 8.38, and 5), with varying concentrations of NaOCl to find the rate of the reaction. It was also performed under three different temperatures to find ΔH . This will be aided by using the UV-Visible Spectrophotometer to record the absorption of color over time as the red solution eventually becomes yellow as $\text{Fe}(\text{Phen})_3^{2+}$ oxidizes to a Hydroxy Bridged Iron Dimer. It is found that the lower the pH, the higher the rate of the reaction occurs.

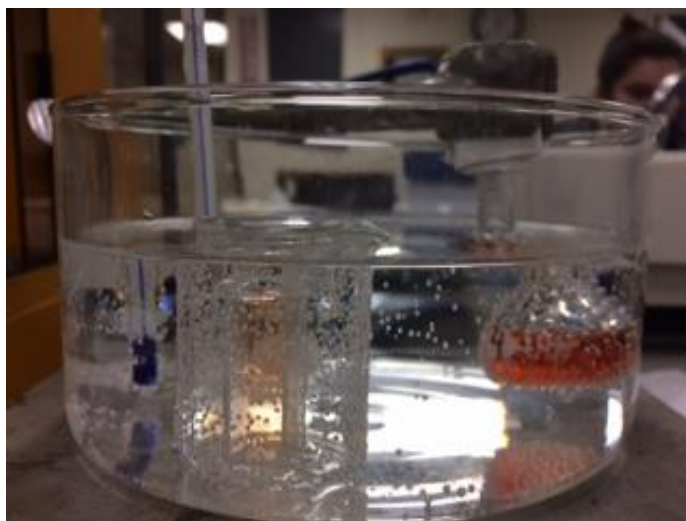
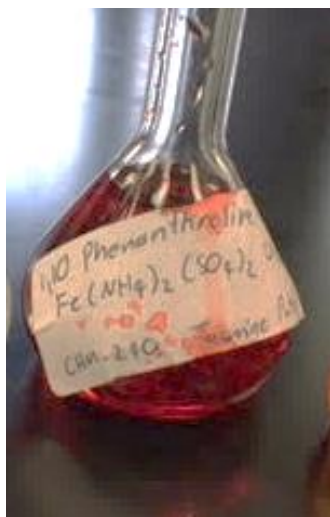
Experimental Section:

Instrumentation: UV-Visible Spectrophotometer and a pH Meter.

Preparation: The first steps of this lab would be to synthesize in-situ 3.1 equivalents of 1,10-Phenanthroline and 1 equivalent of Iron (II) Ammonium Sulfate. Using about 17.9 mg of Iron and 31 mg of Phen, they are placed in a 50 mL volumetric flask with deionized water, creating a deep red color with molarity of 1×10^{-3} . Due to its high concentration when placed in the spectrometer, it was decided to use only a small amount during the runs. When titrating the bleach using the methods given in reference and calculating the density of the commercial bleach, the overall molarity of NaOCl was found to be 1.33. However, the percentage calculated (9.93%) was much higher than what was reported (8.25%). For creating the buffer solutions, first two separate stock solutions needed to be made, 1 M of Na_3BO_3 and 2 M of Na_2SO_4 . After synthesizing the two solutions, each buffer was then made using 0.25 mL of the Sodium Borate solution and 1.25 mL of the Sodium Sulfate. Placing them in a 25 mL volumetric flask and filling it nearly to the top with

Deionized Water, the solution is then placed in a beaker, where it's pH will be measured. Using a pipette to slowly drop H_2SO_4 one drop at a time, to get to the desired pH. This procedure is done for all three pH Buffers.

To find the exact concentrations for the change of absorption over time, Beer's Law was applied. After creating 5 different concentrations of the Iron concentrations and running through the spectrometer, these calculations are then used to plot a calibration curve, Absorption over Concentration. Taking the trend line through zero, the slope found will be the Molar Absorptivity, used to find the concentration when given the absorption.



$$k_{\text{obsd}} = k_0 + \frac{k_1 [\text{H}^+]/K + k_2 [\text{Cl(I)}]}{[\text{H}^+]/K + 1}$$

The pseudo-first order rate constant concluded by the authors.

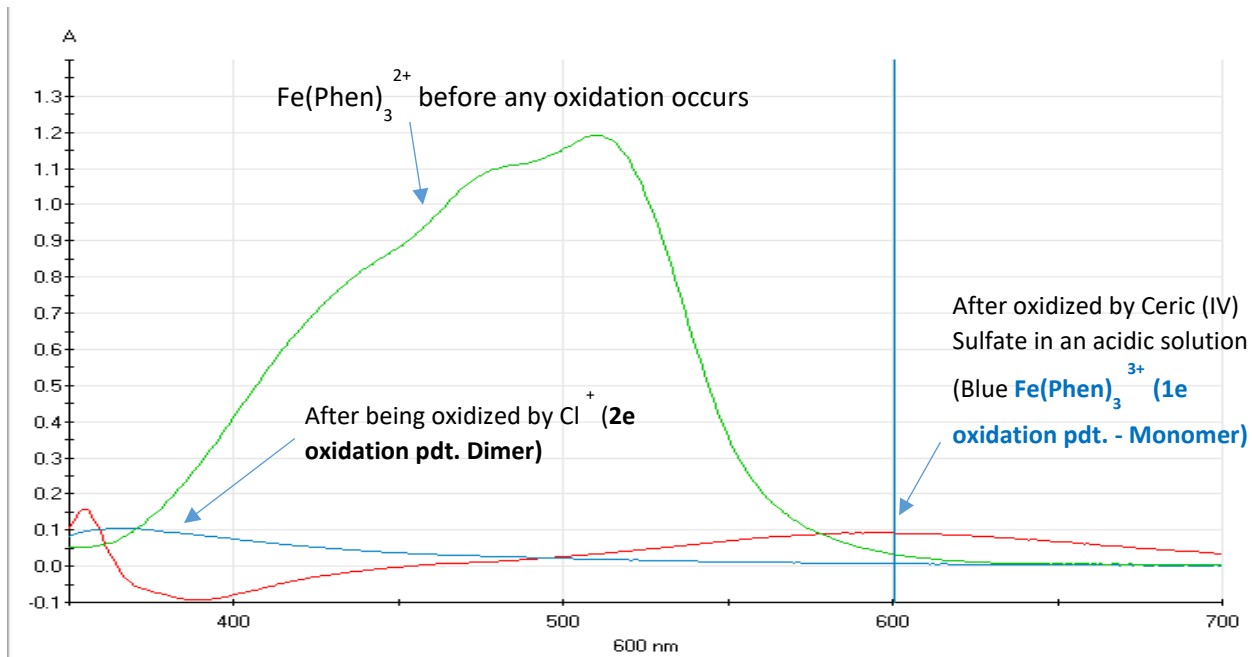
k_0 representing rate of dissociation

k_1 and k_2 are independent of dissociation

K is the acid dissociation constant of HOCl.

Reported to be 2.9×10^{-8}

UV-Visible Characteristics



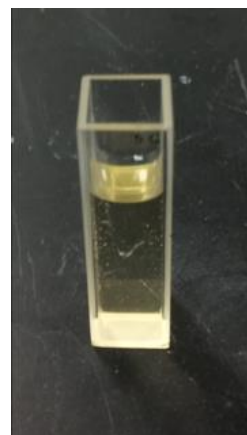
Kinetics of Formation: Performed using the spectrophotometer, the baseline is typically composed of 2.7 mL of Buffer solution, 0.3 mL of Deionized water, and 0.3 mL of Bleach. The 1st run to occur will have 2.7 mL of Buffer and 0.3 mL of Fe(Phen)_3^{2+} . Once the bleach is injected and the oxidation has been completed, there will be a shoulder around 360 nm, a characteristic of the dimer product, and an isobestic point at 390, showing the reaction going smoothly. When plotting the natural log of the concentration vs time, the slope is concluded to be the k_{obsd} based on the fact this is under pseudo-first order conditions.

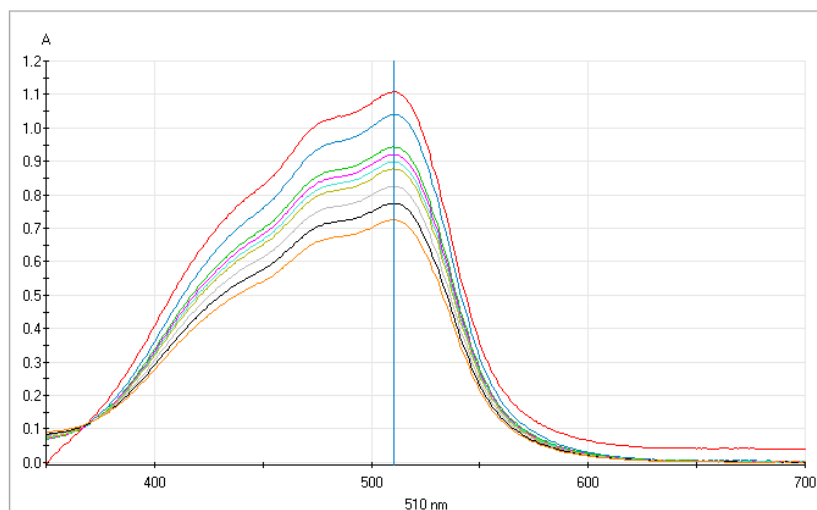
$$[C] = \text{Abs}/10467$$



← Before Oxidation by Cl^+

After Oxidation →



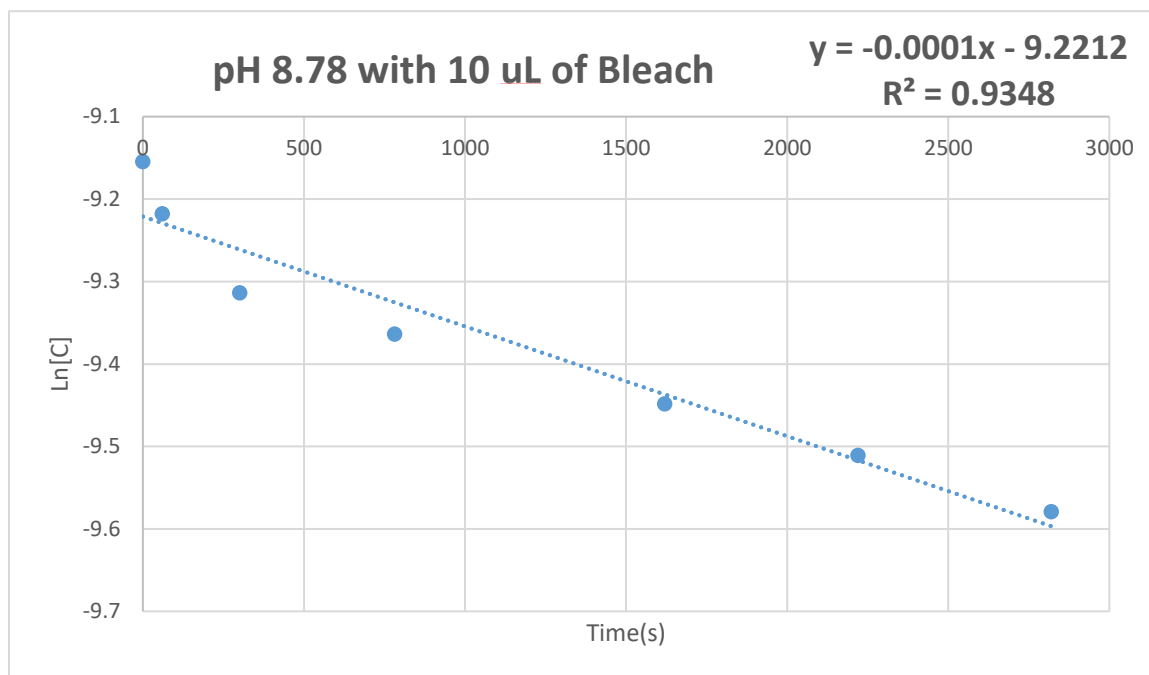


Kinetic Runs with pH 8.78 with 4.43×10^{-3} M of NaOCl

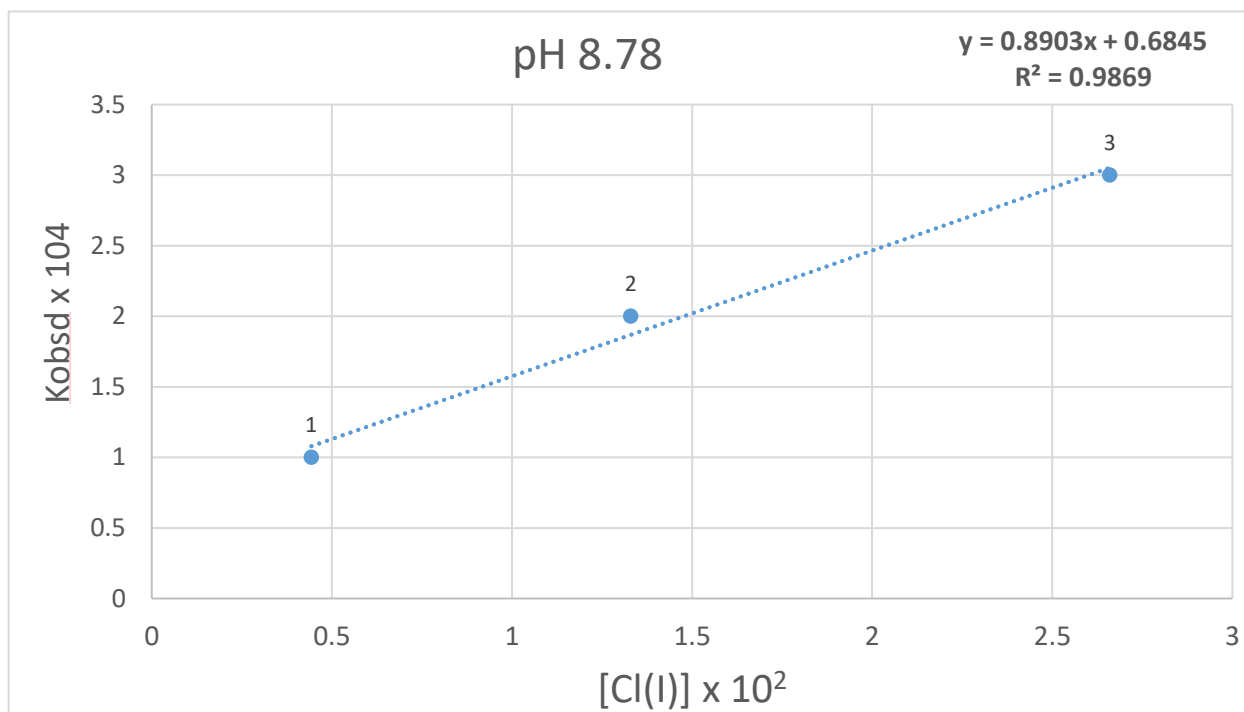
$$\ln [C] = -kt + \ln[C_0]$$

Abs	[C]	Time (s)	Ln[C]
1.107	0.000106	0	-9.15433
1.039	9.93E-05	60	-9.21772
0.944	9.02E-05	301	-9.31361
0.898	8.58E-05	781	-9.36357
0.825	7.88E-05	1620	-9.44835
0.775	7.4E-05	2220	-9.51087
0.724	6.92E-05	2820	-9.57895

$$K_{\text{obsd}} = 1 \times 10^{-4} \text{ M}$$



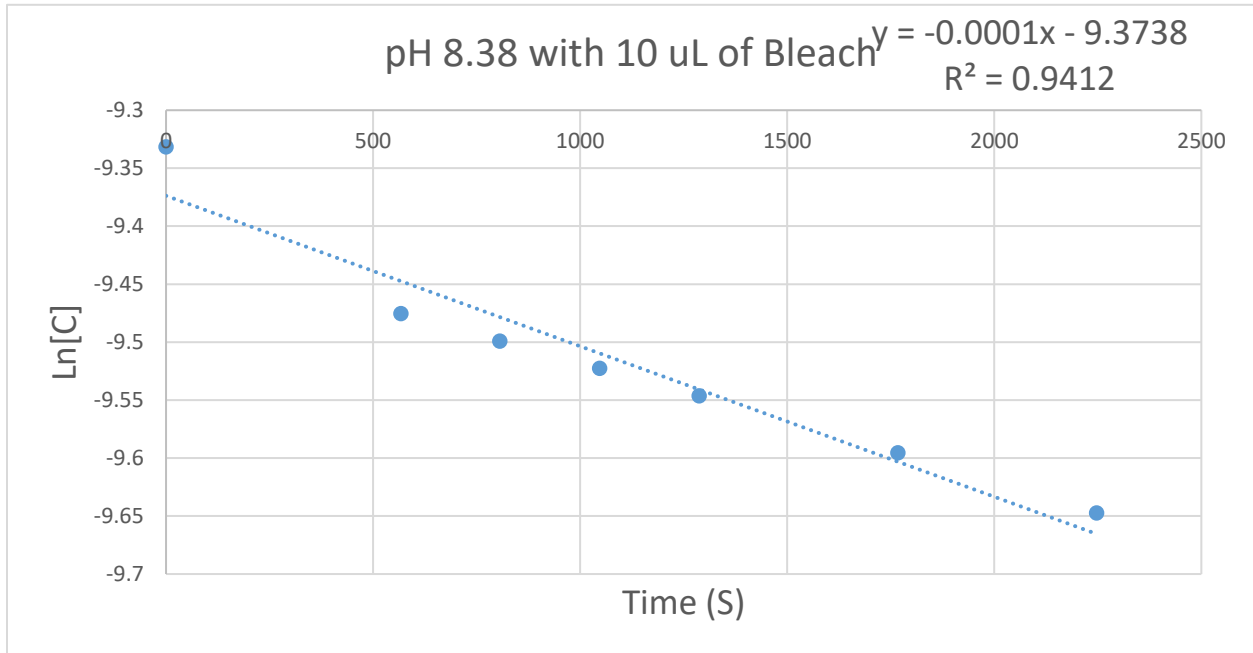
Plot of K_{obsd} vs. $[\text{Cl}^+]$ (0.443 , 1.33 , and $2.66 \times 10^{-2} \text{ M}$ corresponds to 10 , 30 , and 60 uL of Bleach)



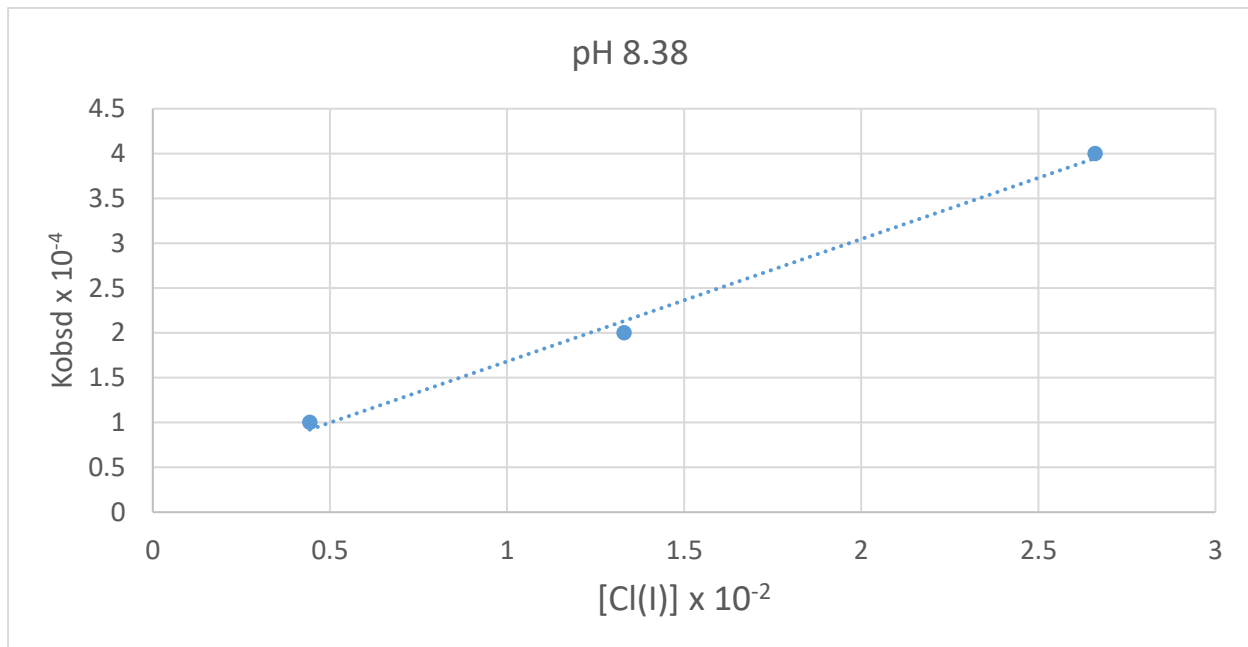
Kinetic Runs with pH 8.38 with 4.43×10^{-3} M of NaOCl

$$\ln [C] = -kt + \ln[C_0]$$

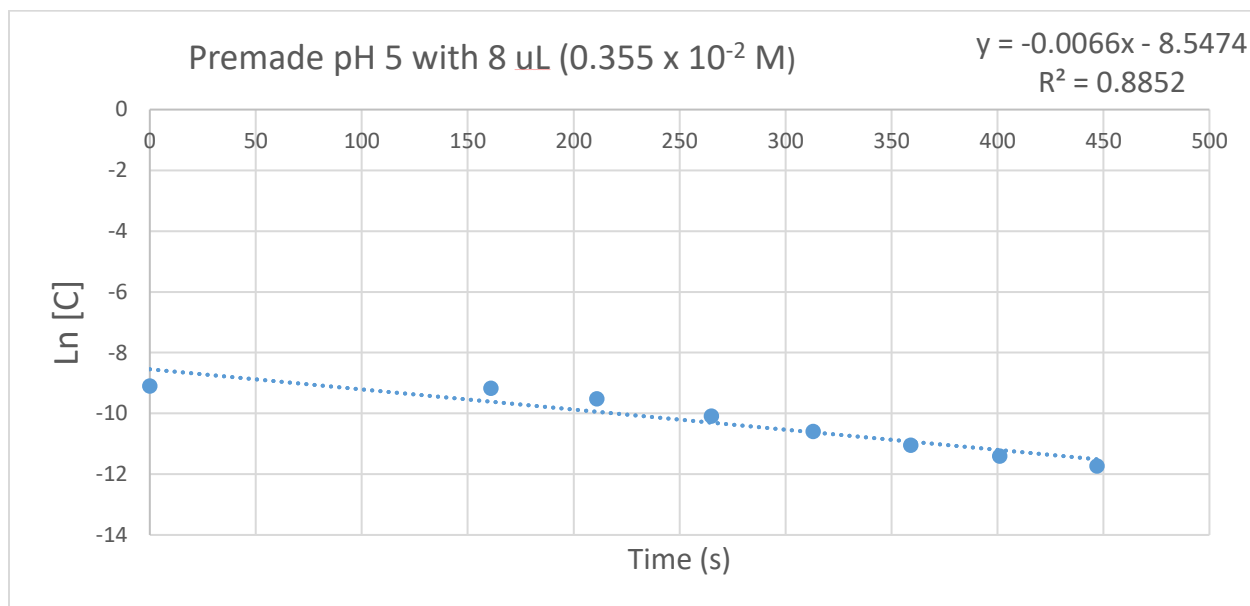
$$K_{\text{obsd}} = 1 \times 10^{-4} \text{ M}$$



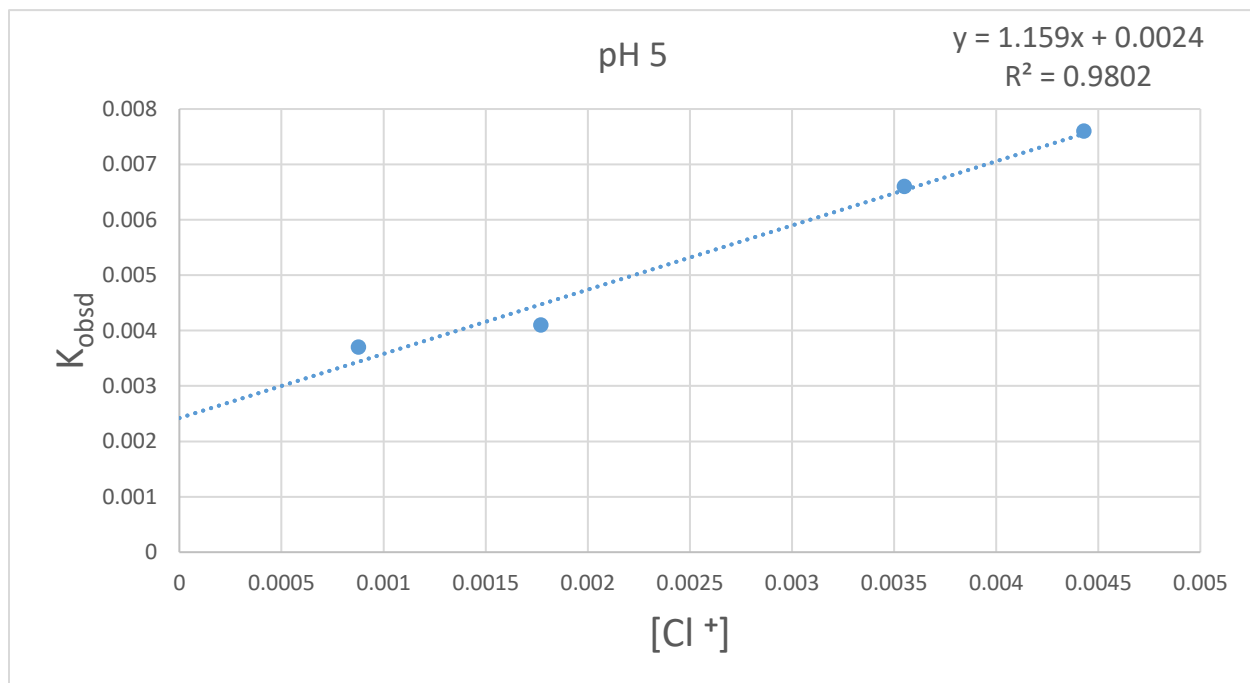
Plot K_{obsd} vs. $[\text{Cl}^+]$ (4.43×10^{-3} , 1.33×10^{-2} , and 2.66×10^{-2} M correspond to 10, 30, and 60 μL of Bleach respectively) for pH 8.38.



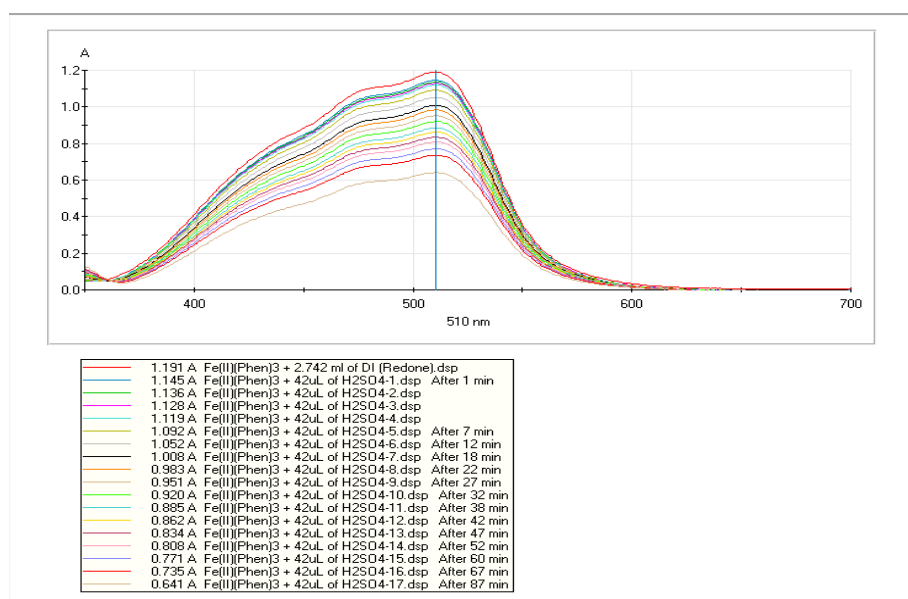
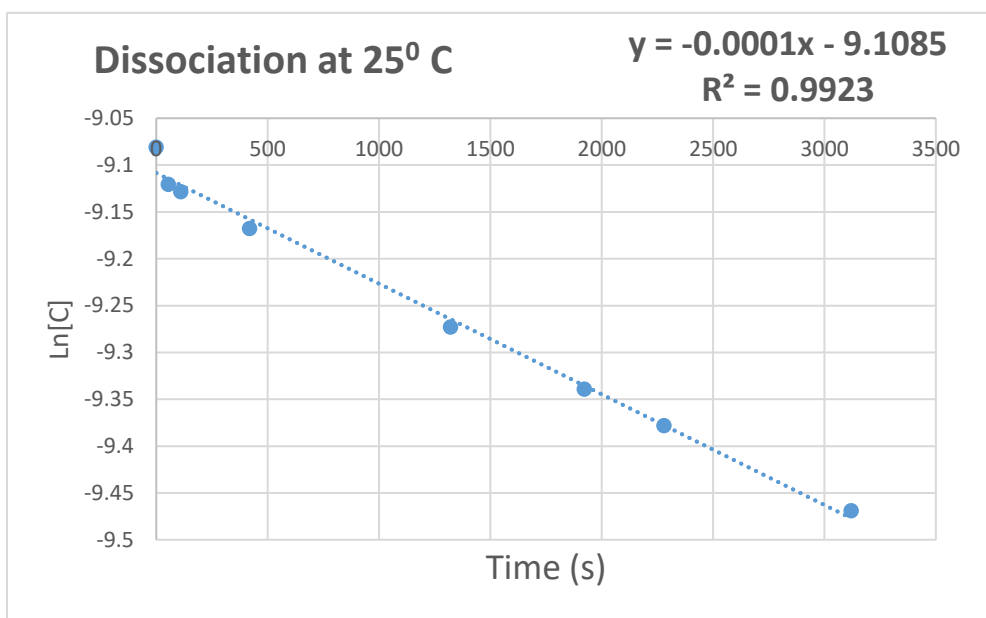
Simplified Rate: At pH 5, the pseudo-first order conditions are simplified to $k_{\text{obsd}} = k_0 + k_1[\text{Cl}^+]$



From this slope, the k_0 appears to be 0.0024 s^{-1} and k_1 is 1.159 s^{-1}



Dissociation in 0.5 M of H₂SO₄: To ensure that the k_0 value found from pH 5 is correct, finding the observed rate of reaction in H₂SO₄ will ensure the value is correct, due to no other possible reactions occurring at the same time. With no buffer or bleach, the baseline contains 3 mL of water and 42 uL of H₂SO₄ (0.5 M). The first run would have 2.7 mL of water and 0.3 mL of Fe(Phen)₃²⁺, and then, similar to an oxidation, 42 uL of the acid is injected when the timer starts and then run through the spectrometer as soon as possible. Then proceed to run scans as often as deemed necessary. The rate of dissociation at room temperature was concluded to be $1 \times 10^{-4} \text{ s}^{-1}$.



Determining ΔH : The change in enthalpy, ΔH can be found by first finding the average k equivalent value from each temperature. To do this, first the reaction needs to be performed and observed at two other temperatures, 40 and 15^o C. The reaction performed at a higher temperature is notably faster than at lower temperatures. Once the information is recorded and k_{eq} is found, then it is necessary to plot it's natural log against 1/T. The slope will be the ΔH .

When performing the reactions at different temperatures, a water bath was used to keep the cuvette at the necessary temperature as well as the solution so there would be no concerns about equilibrating.

Dissociation in H₂SO₄ at 25^o C
 $K_{eq} = 5.796 \times 10^{-6}$

$$K_{eq} = \frac{[(Abs_0 - Abs_f) / 10467]^2}{Abs_f / 10467}$$

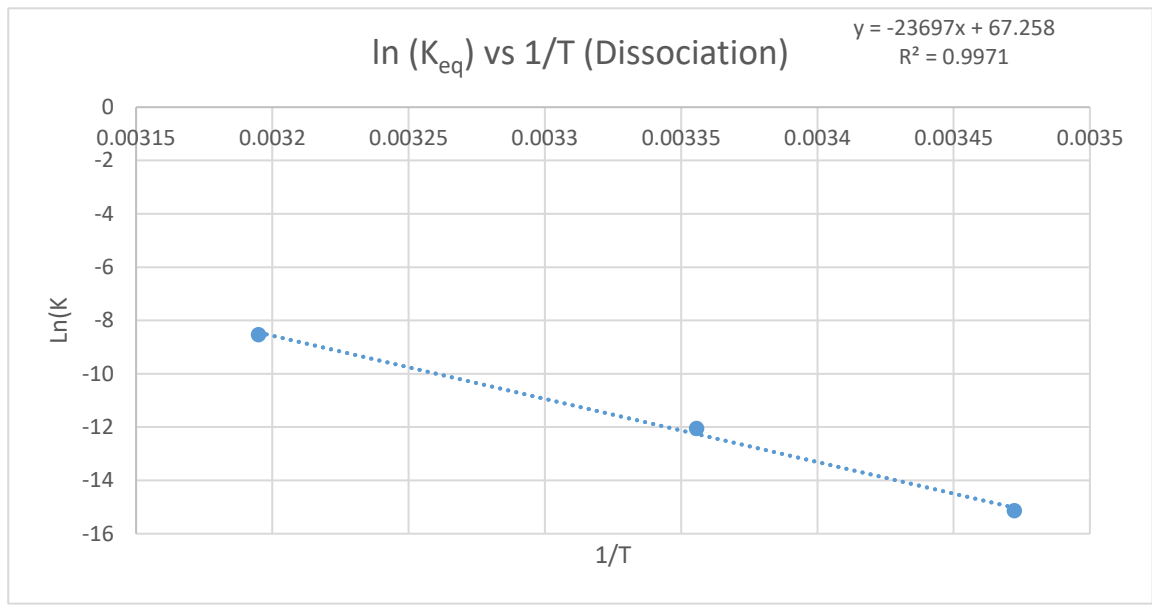
Abs			
1.191	$[(Abs_0 - Abs_f) / 10467]^2$	Absf/10467	k
1.145	1.9314E-11	0.00010939	1.76558E-07
1.136	2.76109E-11	0.00010853	2.54405E-07
1.092	8.94594E-11	0.00010433	8.57483E-07
0.983	3.94896E-10	9.3914E-05	4.20485E-06
0.92	6.70338E-10	8.7895E-05	7.62656E-06
0.885	8.5467E-10	8.4551E-05	1.01083E-05
0.808	1.33892E-09	7.7195E-05	1.73446E-05

Dissociation in H₂SO₄ at 40^o C
 $K_{eq} = 1.961 \times 10^{-4}$

Abs	k
0.936	0
0.733	5.371E-06
0.529	2.992E-05
0.35	9.374E-05
0.253	0.0001762
0.17	0.0003298
0.118	0.0005418

Dissociation in H₂SO₄ at 15^o C
 $K_{eq} = 2.656 \times 10^{-7}$

Abs	k
1.192	0
1.178	1.5896E-08
1.173	2.9403E-08
1.139	2.3562E-07
1.129	3.3587E-07
1.119	4.5498E-07
1.114	5.2177E-07

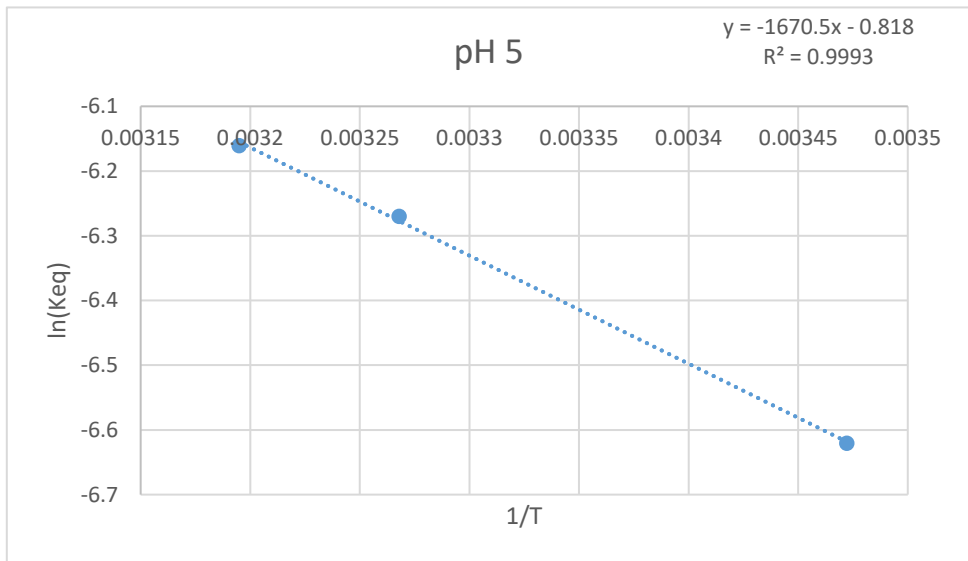


$$\ln K_{eq} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

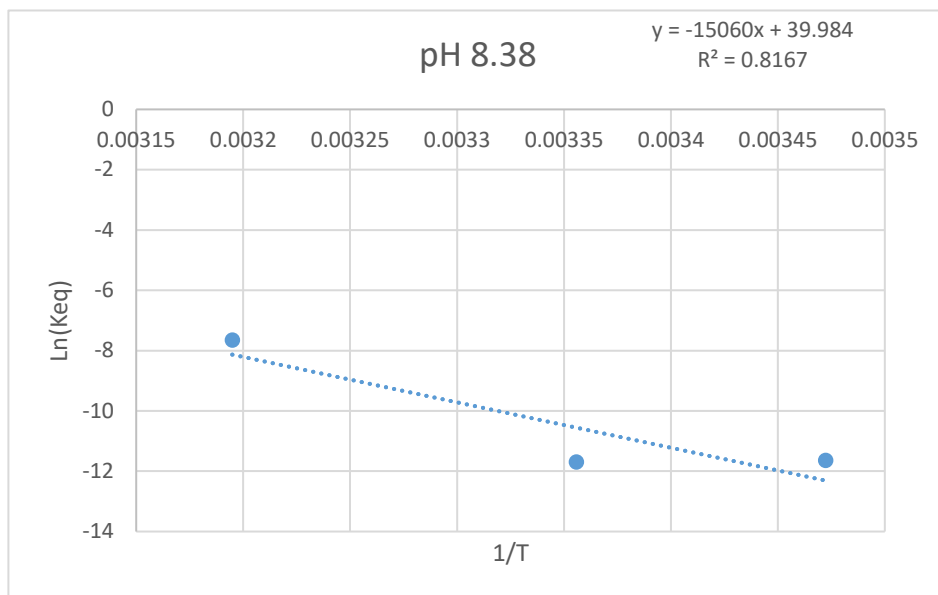
1/T	0.003472222	0.003356	0.003195
ln(K _{eq})	-15.14131534	-12.0583	-8.53681

ΔH in regards to dissociation is 197 kJ/mol (47.1 kCal/Mol)

ΔH for pHs 8.38 and 5: Performed in the same manner as the same manner as the dissociation in H₂SO₄ when finding ΔH and controlling the temperature of the solution.



$\Delta H = 3.31$ kJ/Mol
 0.791 kCal/Mol



$\Delta H = 125.2 \text{ kJ/Mol}$
 29.9 kCal/Mol

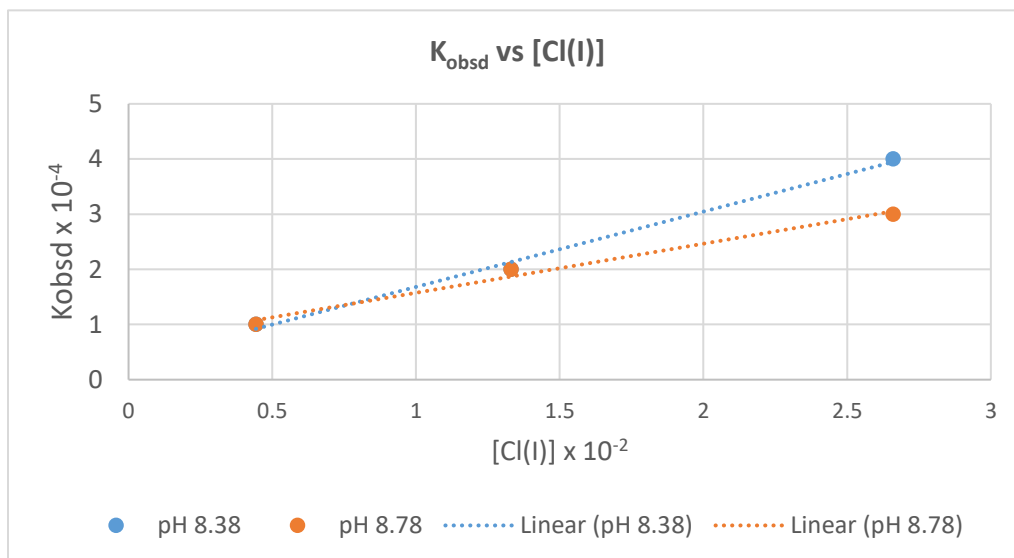
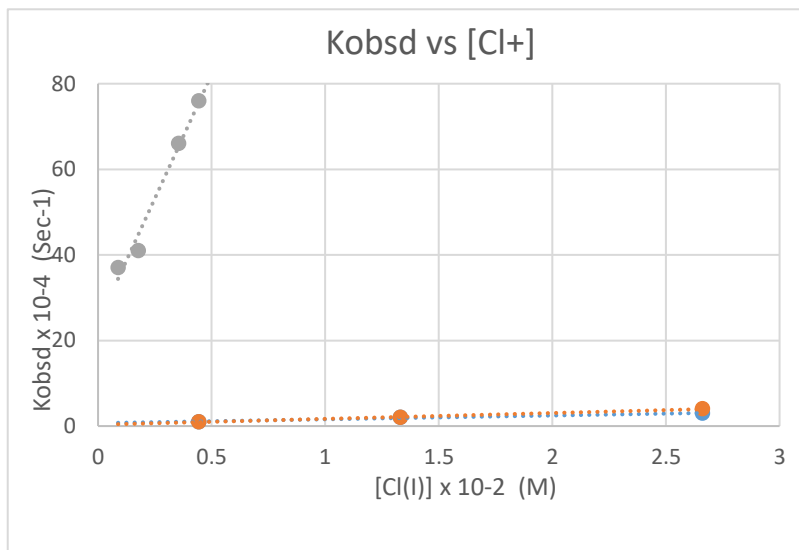
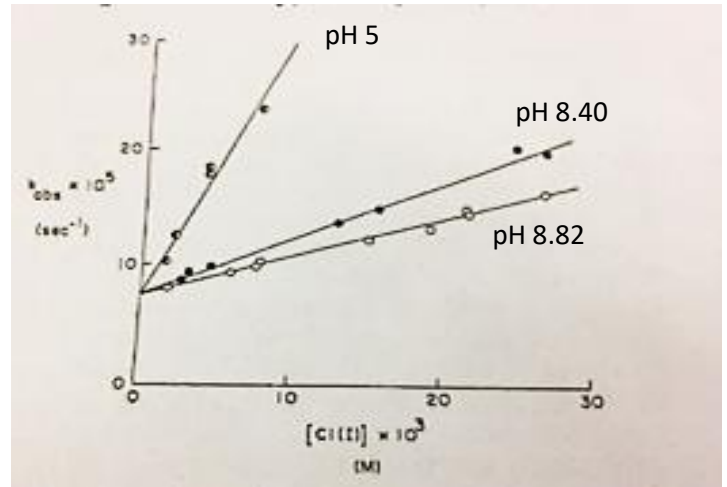
At pH 5, ΔH is found in regards to k_1 and at pH 8.4 it is found for k_2 .

Calculating k values: From previous plots, the k values can be easily seen. The k_{obsd} is objective depending on the pH and concentration of Cl^+ , k_0 is found upon the slope in the dissociation in H_2SO_4 , and k_1 is found to be $1.156 \text{ M}^{-1} \text{ s}^{-1}$ based upon the slope for pH 5 because of the simplified rate law. K is the 2.9×10^{-8} , the acid dissociation constant for HOCl.

Using this information, k_2 can be calculated to be $7.71 \text{ M}^{-1} \text{ s}^{-1}$.

Comparisons between Literature Values and Found Values.

In similarity to the literature values, pHs of around 8.4 and 8.82 have close k_{obsd} values to each other, as well as pH 5 having higher rates with less concentration.



A better view of pH 8.38 and 8.78, due to their k_{obsd} values being close to one another.

	Literary Value	My Values
k_0	$7.5 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$	$1 \times 10^{-4} \text{ s}^{-1}$
k_1	$2.2 \pm 0.14 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$	$1.159 \text{ M}^{-1} \text{ s}^{-1}$
k_2	$2.0 \pm 0.16 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$	$7.71 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$
ΔH (in regards to k_d)	$30.2 \pm 0.3 \text{ kCal / Mol}$	47.1 kCal/Mol
ΔH (in regards to k_1)	$16.2 \pm 2 \text{ kCal / Mol}$	0.791 kCal/Mol
ΔH (in regards to k_2)	$25.3 \pm 2.5 \text{ kCal/Mol}$	29.9 kCal/Mol

Results and Discussion:

As it can be seen, my values on the rate of reaction have shown to be higher than the literature values. While they do appear to be in relatively close range to one another, my k_1 has shown to be and its change in enthalpy have shown to be about 50 times higher than what was initially calculated, while in reverse my ΔH in respect to k_1 is 1/20th out of the literature.

Aside from these oddities, overall my values are shown to be higher. It is theorized that there is possibly Cl_2 gas in the bleach, which is a strong oxidizing agent. When discovering this possibility, it has come across as ironic, as in the published lab, it was performed in the pH range of 2-9, to eliminate such chlorine interference with HOCl. While my values are not quite the same as those published, this possibility as well as the similar characteristics of the reaction have lead me to believe that this experiment was done to the best of my abilities with this type of setting.

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References:

General Chemistry Book, 10th Edition. Author: Raymond Chang. Pages 156-159

“The reaction of Tris (1,10-Phenanthroline) Iron(II) Ion with Chlorine(I) Species” by Martin G. Ondrus and Gilbert Gordon Inorganic Chemistry, 1971, Vol. 10, pg 474-477