



Kinetics of Aquation of Hexakis (Urea) Chromium (III) Chloride

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Abstract

Chromium hexaurea complex was synthesized and characterized by two different spectroscopic techniques. The UV-Vis spectra showed a maximum absorbance at 290nm while IR spectra showed $\nu(C=N)$ stretching vibration in the free urea occurred at 1681cm^{-1} but shifted down to 1633cm^{-1} in the complex a change of 48cm^{-1} indicating a bonding to nitrogen, The kinetics of the aquation of Hexakis (urea) chromium (III) chloride complex has been shown to follow first order kinetics with average rate constant k_{obs} (25°C , 40°C and 50°C) to be 2.5×10^{-2} , 3.04×10^{-2} and 3.3×10^{-2} respectively and the corresponding activation parameters of $\Delta H^* = +5.19\text{kJK}^{-1}$, $\Delta S^* = -258\text{JK}^{-1}$ and $\Delta G^*_{25} = 82.25\text{kJK}^{-1}$, $\Delta G^*_{40} = 85.62\text{kJK}^{-1}$, $\Delta G^*_{50} = 88.199\text{kJK}^{-1}$ indicative associative mechanism.

Keywords: Order of reaction, reaction mechanism, synthesis, rate constant, Eyring plot, activation parameters.

Introduction

German scientist Ludwig Ferdinand .W. was the first to carry out a quantitative study in chemical kinetics. He used polarimetry to investigate the acid-catalyzed conversion of sucrose. Wilhelmy depicted that the reaction rate (dZ/dt) was proportional to the concentration of sucrose (Z) and acid (S) according to the differential equation: $-dZ/dt = MZS \Rightarrow \log Z = -MSt + C$, where M is the transformation coefficient of sucrose, which is related to the unit of time, i.e., the reaction rate constant and C is the constant of integration¹. Chemical kinetics is the study of the rates of chemical reactions. Such studies are closely related to the development and understanding of reaction mechanisms.

It is well known that chemical kinetics and reaction mechanisms are often regarded as synonymous and provide information on reaction mechanisms. The importance of the value of rate of constant cannot be over-emphasized since it helps to determine the value of the rate of any reaction applying its rate equation.

The knowledge of chemical rate equation is very vital industrially, in establishing the optimum conditions of pressure, temperature, feed composition, space velocity, extent of conversion and recycling^{2,3}. In studying a chemical reaction, it is essential to ascertain not only the chemical characteristics of the reactants, but also the optimum condition in which the reaction takes place, the mechanism, the rate by which it occurs, and the equilibrium toward which it proceeds. By the law of mass action, chemical rate of reaction at a constant temperature relies vividly on the concentrations of the substances that affects the rate. This research was centered on chromium Hexa urea chloride derived from hydrated chromium (III) chloride and urea.

Materials and methods

The purity of the chemicals to be used were taken into consideration by using only reagent analytical grades (AR). They include hydrated chromium (III) chloride, Urea, ethanol, P-dimethylaminobenzaldehyde.

Preparation of solutions: 0.4M of HCl: 3.3ml of HCl (37%) was pipette in a 100ml volumetric flask and made up to volume with distilled.

5M of ethanol: Was prepared by dilution using the formula $C_1V_1 = C_2V_2$

Where: C_1 =specific gravity of ethanol (17.14), C_2 = molarity of ethanol (5M), V_2 = 500 ml, V_1 = final volume of ethanol, $V_1 = C_2V_2/C_1$, $V_1 = 5 \times 500/17.14$, $V_1 = 146\text{ml}$.

146ml of ethanol were measured into volumetric flask of 500 ml and diluted with distilled water to mark.

2.1M Urea: (H_2NCONH_2) 12.6g of urea was weighed and transferred to volumetric flask of 100 ml and measured to mark with distilled water.

2mM of chromium hexaurea: 0.026g of the complex is weighed and transferred to a 25ml volumetric flask and make up to mark with distilled water
2mM of p-dimethylaminobenzaldehyde: 0.0075g of p-dimethylaminobenzaldehyde was weighed and transferred to 25ml volumetric flask and make up to the mark with distilled water.

Synthesis of Chromium Hexa Urea Chloride complex $[\text{Cr}(\text{H}_2\text{NCONH}_2)_6]\text{Cl}_3$: Modified literature method by Pfeiffer⁴ was used. Hydrated chromium (III) chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4g,

0.020mol), urea (7.3g, 0.122mol) and ethanol (20.0ml) were taken in a round-bottomed flask (100ml) and heated under reflux with constant stirring on a water bath for about 45 minutes.

The green solution was filtered hot through a filter paper with no residue. The filtrate was concentrated on a water-bath then finally allowed to cool in air. Within one hour, a green precipitate was obtained. It was filtered, washed with the supernatant and dried in air. Yield: 0.99g, 14.9%.

Preparation of coloured reagent of p-dimethyl aminobenzaldehyde: Urea (2.1g, 0.122mol) was prepared and mixed with 0.4M of hydrochloric acid; 5M ethanol was prepared and mixed with 25ml of 2mM of p-dimethyl aminobenzaldehyde. A yellow solution was obtained.

Results and discussion

The initial dark green of (CrCl₃) changed to light green depicting the formation of a new complex and a white ligand was observed. The observe rate constant of the aquation of chromium hexaurea complex was found to be 2.5×10^{-2} , 3.04×10^{-2} and 3.3×10^{-2} at temperature 25°C, 40°C and 50°C respectively.

The corresponding activation parameters as determined from the Eyring plot, were enthalpy of activation $\Delta H^* = +5.188\text{kJ}$, the entropy of activation $\Delta S^* = -258.6\text{JK}^{-1}$ and $\Delta G^*_{25} = 82.25\text{kJK}^{-1}$, $\Delta G^*_{40} = 85.629\text{kJK}^{-1}$, $\Delta G^*_{50} = 88.199\text{kJK}^{-1}$. The positive value of enthalpy indicate an endothermic reaction. The negative value of the entropy of activation ΔS^* that has been calculated for the system suggest an associative mechanism, the negative entropy of activation however suggest the formation of more structured transition state from the less organized reactant. The reaction is an endothermic reaction since the value of enthalpy is positive.

From literature the exchange of DMSO with Cr[DMSO]³⁺ was found to be characterized by a first order rate constant at 75°C with activation parameter as $\Delta H^* = 23.1\text{kcal}$, $\Delta S^* = -11.8\text{ kmol}^{-1}\text{K}^{-1}$ and $\Delta V^* = -11.3$. The reaction was suggested to follow an associative interchange mechanism. Similar conclusion were reached in the reaction between [Cr(H₂O)]³⁺ with glycine.

Infrared spectral: The coordination of the metal (Cr³⁺) to the ligand was evident as seen in the infrared spectra in Table-1. The infrared spectrum of the free urea was compared with that of the complex to determine the coordination sites that may have involve in the bonding.

Upon comparison, it was observed that the ligand was principally coordinated to the metal atom in the following ways; It was found that C=N stretching vibration in the free urea occurred at 1681cm⁻¹ but in the complex has shifted down to 1633cm⁻¹ in the complex, a change of 48cm⁻¹ indicating a bonding to nitrogen. A band appearing at 3500.6cm⁻¹ due to O-

H vibration in the free urea was not found in the spectra of the metal complex. While the band at 541cm⁻¹ is due to the metal bond to urea in the complex. The C=O band in free urea shifted down from 666cm⁻¹ to 630.9cm⁻¹. In characterizing a compound, we basically compare the IR spectra of the free ligand to that of the metal complex.

Typically we look for the change in the stretching vibrations of OH, CO from the carbonyl compounds, NH, SO etc. in the complex. The complex [Cr(H₂NCONH₂)₆]Cl₃ used in this study the ligand has two donor atom O and N. The IR of the complex did not show any reasonable changes for the stretching vibration (ν) for NH in the 3000cm⁻¹ region when compared with that of free urea. This has ruled out bonding through N.

However, in the free urea occurred at 1606cm⁻¹ but in the complex, it shifted down to 1556.66cm⁻¹ a change of 50.3cm⁻¹ and thus confirmed bonding through oxygen.

Electronic Spectral: The characterization of the complex of chromium (III) as an oxygen bound compound is supported by the UV-VIS spectra ($\lambda_{\text{max}}=290\text{nm}$) see Figure-3. Maximum absorbance were obtained at 290nm, 450nm and 650nm.

Table-1: IR Spectra analysis of free Urea and Chromium hexaurea complex.

Functional group	Free urea	Cr(NH ₂ CONH ₂) complex
O-H	3500	3438.6
C=C	2820	
C=N	1681	1633.8
C=O	666	630.9

Kinetic measurement of hexakis (urea) chromium (III) chloride complex at different temperature (25°C, 40°C, 50°C): The experimental results obtain from the kinetic measurement of chromium hexaurea complex are presented in the tables. Table-2 and 3, shows the results of the kinetic measurement at room temperature (25°C). Table-4 and 5, shows the result of the kinetic measurement at (40°C). Table-6 and 7 represent the kinetic measurement at 50°C.

The Rate Constant Determination at 25°C, 40°C and 50°C of the Aquation of Hexakis (urea) chromium (III) Chloride Complex: Determination of the rate constant for the aquation of chromium (III) complex at 25°C.: Results of first experiment are mention in Table-2 and Figure-1. Results of second experiment are mention in Table-3 and Figure-2.

Table-2: Kinetic measurement at 25⁰C.

Time (min)	Absorbance A	A _∞ - A _t	log(A _∞ - A _t)
0	0.065	0.024	-1.619
5	0.068	0.021	-1.678
10	0.069	0.02	-1.699
20	0.073	0.016	-1.795
25	0.075	0.014	-1.854
35	0.079	0.01	-2.00
45	0.081	0.008	-2.097
55	0.085	0.004	-2.398
65	0.086	0.003	-2.523
75	0.088	0.001	-3.00
85	∞	∞	∞

Table-3: Kinetic measurement at room temperature at 25⁰C.

Time(min)	Absorbance A	A _∞ -A _t	log(A _∞ - A _t)
0	0.085	0.045	-0.915
5	0.087	0.043	-1.367
10	0.093	0.037	-1.432
20	0.095	0.035	-1.456
30	0.097	0.033	-1.481
40	0.111	0.019	-1.699
55	0.112	0.018	-1.745
70	∞	∞	∞

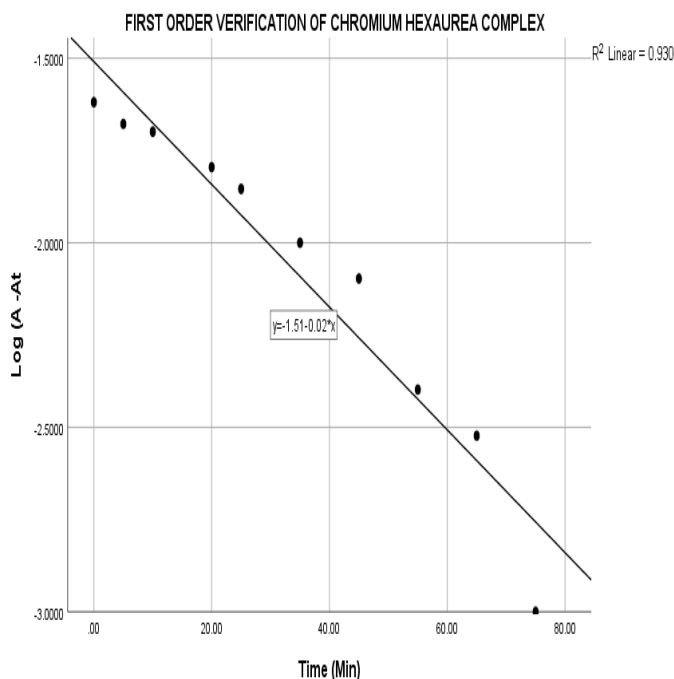


Figure-1: The graph of log (A_∞-A_t) vs Time (t).

$$k_{obs} = \text{Slope} \times 2.303$$

$$\text{Slope} = 0.0145$$

$$k_{obs} = 0.00145 \times 2.303 = 0.0334$$

$$k_{obs} = 3.34 \times 10^{-2}$$

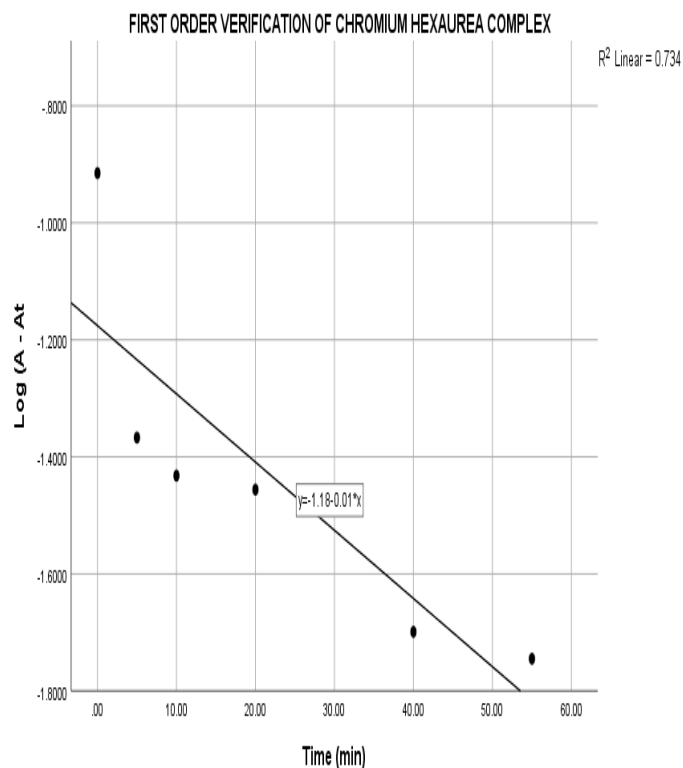


Figure-2: Graph of log (A_∞-A_t) vs Time (t).

$$k_{obs} = \text{Slope} \times 2.303$$

$$\text{Slope} = 0.007$$

$$K_{obs} = 0.007 \times 2.303 = 0.0162 = 1.62 \times 10^{-2}$$

Average K_{obs} at 25⁰C

$$= 3.34 \times 10^{-2} + 1.62 \times 10^{-2} / 2$$

$$= 0.04960 / 2 = 0.0248 = 2.5 \times 10^{-2}$$

Determination of the rate constant for the aqution of chromium (III) complex at 40°C: Results of first experiment are mention in Table-4 and Figure-3. Results of second experiment are mention in Table-5 and Figure-4.

Table-4: Kinetics measurement at temperature 40°C.

Time(min)	Absorbance A	$A_{\infty} - A_t$	$\log(A_{\infty} - A_t)$
0	0.322	0.01	-2.00
5	0.323	0.009	-2.05
15	0.324	0.008	-2.096
25	0.326	0.006	-2.22
35	0.327	0.005	-2.30
45	0.329	0.003	-2.52
55	0.330	0.002	-2.698
65	∞	∞	∞

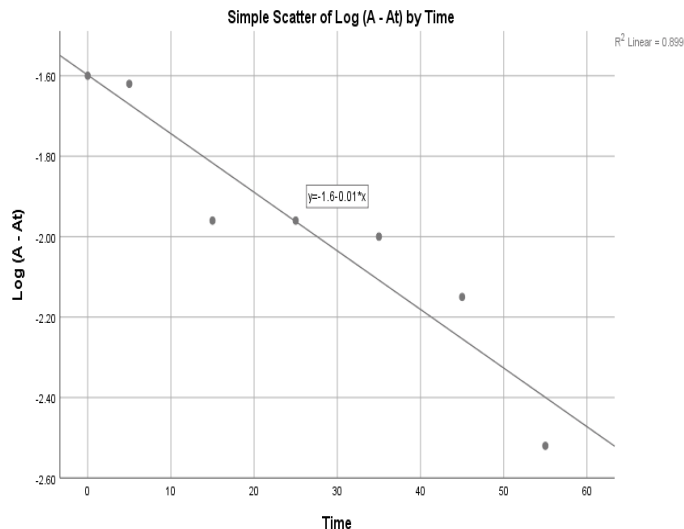


Figure-4: The graph of $\log(A_{\infty} - A_t)$ vs Time (t).

$$K_{obs} = \text{Slope} \times 2.303$$

$$K_{obs} = 0.02 \times 2.303 = -0.00434 = 4.61 \times 10^{-2}$$

$$\text{Average } K_{obs} \text{ at } 40^{\circ}\text{C} \\ = 1.48 \times 10^{-2} + 4.61 \times 10^{-2} / 2 = 0.0608 / 2 = 0.0304.$$

Determination of the rate constant for the equation of chromium (III) complex at 50°C: Results of first experiment are mention in Table-6 and Figure-5. Results of second experiment are mention in Table-7 and Figure-6.

Table-6: Kinetic measurement at 50°C.

Time(min)	Absorbance A	$A_{\infty} - A_t$	$\log(A_{\infty} - A_t)$
0	0.221	0.015	-1.82
5	0.223	0.013	-1.89
10	0.224	0.012	-1.92
20	0.225	0.011	-1.96
30	0.226	0.01	-2.00
40	0.227	0.009	-2.05
50	0.230	0.006	-2.22
60	0.232	0.004	-2.40
70	0.234	0.002	-2.70
80	0.235	0.001	-3.00
90	∞	∞	∞

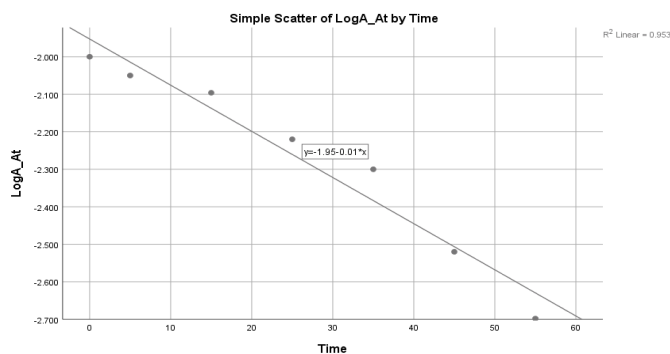


Figure-3: The graph of $\log(A_{\infty} - A_t)$ vs Time (t).

$$k_{obs} = \text{Slope} \times 2.303$$

$$k_{obs} = 0.01476 \times 2.303 = 1.48 \times 10^{-2}$$

Table-5: Kinetics measurement at temperature 40°C.

Time(min)	Absorbance A	$A_{\infty} - A_t$	$\log(A_{\infty} - A_t)$
0	0.185	0.025	-1.60
5	0.186	0.024	-1.62
15	0.199	0.011	-1.96
25	0.199	0.011	-1.96
35	0.200	0.01	-2.00
45	0.203	0.007	-2.15
55	0.207	0.003	-2.52
65	∞	∞	∞

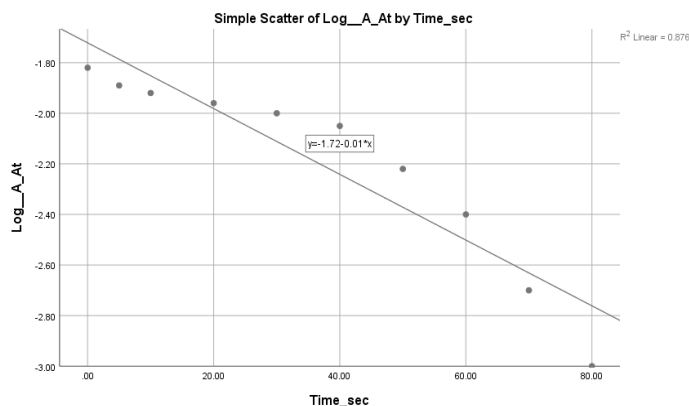


Figure-5: The graph of $\log(A_\infty - A_t)$ vs Time (t).

$$K_{obs} = \text{Slope} \times 2.303$$

$$= 0.0125 \times 2.303 = 0.0287 = 2.87 \times 10^{-2}$$

Table-7: Kinetic measurement at temperature 50°C.

Time(min)	Absorbance A	$A_\infty - A_t$	$\log(A_\infty - A_t)$
0	0.172	0.008	-2.10
5	0.173	0.007	-2.15
15	0.174	0.006	-2.22
25	0.176	0.004	-2.40
35	0.178	0.002	-2.70
45	0.179	0.001	-2.70
55	∞	∞	∞

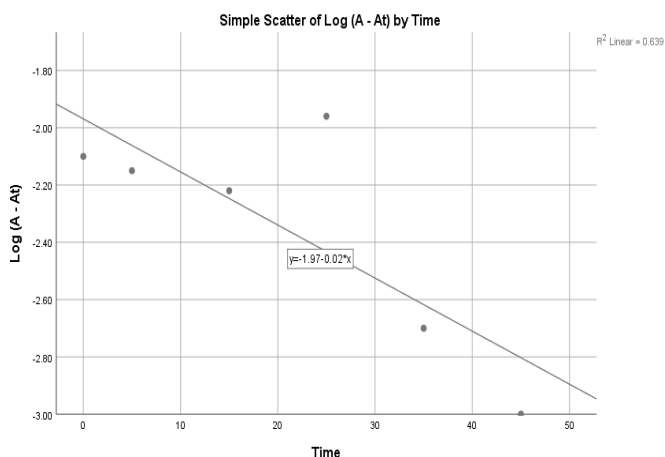


Figure-6: The graph of $\log(A_\infty - A_t)$ vs Time (t).

$$K_{obs} = \text{Slope} \times 2.303$$

$$= 0.01667 \times 2.303 = 0.0384 = 3.84 \times 10^{-2}$$

Average K_{obs} at 50°C

$$= 2.87 \times 10^{-2} + 3.8 \times 10^{-2} / 2$$

$$= 0.0671 / 2 = 0.0336 = 3.3 \times 10^{-2}$$

Table-8: Rate Constants observed at the various temperatures.

Temp (°C)	1 ST	2 nd	Average
25°C	3.34×10^{-2}	1.62×10^{-2}	2.5×10^{-2}
40°C	1.48×10^{-2}	4.6×10^{-2}	3.04×10^{-2}
50°C	2.87×10^{-2}	3.8×10^{-2}	3.3×10^{-2}

Table-9: Data for Eyring plot.

Temperature(T)°K	Kobs	1/T	ln[k/T]
298	2.5×10^{-2}	3.41×10^{-3}	-9.386
313	3.04×10^{-2}	3.21×10^{-3}	-9.241
323	3.3×10^{-2}	3.10×10^{-3}	-9.189

Determination of the enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and free energy of activation (ΔG^*) in the aqution of chromium hexaurea:

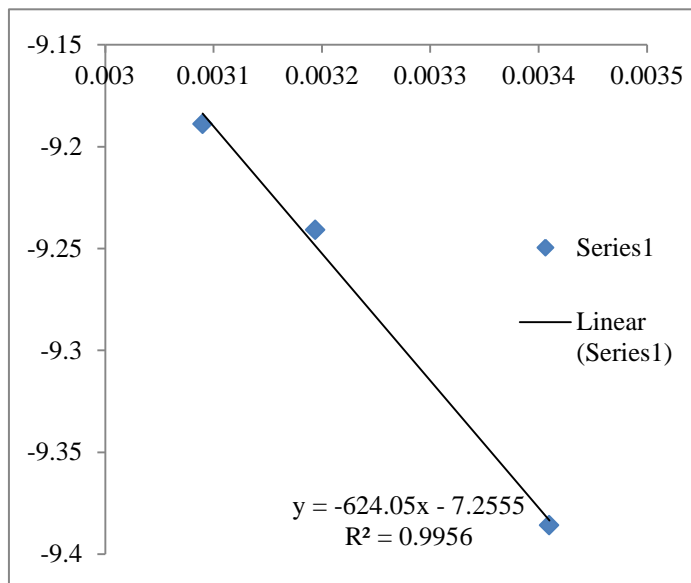


Figure-7: Eyring plot of $\ln [k/T]$ vs $1/T$.

Slope = -624.05
Slope = $\Delta H^* / R$
Where: R = gas constant (8.314)
Therefore, $\Delta H^* = -624.05 \times 8.314$
 $= -\Delta H^* = -5188.4$
 $\Delta H^* = +5.1884 \text{ kJ}$
 $\Delta H^* = +5.1884 \text{ kJ}$

The Entropy of activation can be obtain with the formula,
 Intercept = $\ln k/h + \Delta S^*/R$

Where: k = Boltzmanconstant ($1.381 \times 10^{-23} \text{ Jk}^{-1}$), h = Planck constant ($6.628 \times 10^{-34} \text{ Js}$), R = molar gas constant = $8.314 \text{ Jk}^{-1}\text{mol}$

From the Eyring plot, intercept = -9.105

$$-7.255 = \ln 1.381 \times 10^{-23} / 6.628 \times 10^{-34} + \Delta S^*/8.314$$

$$-7.255 = \ln 1.381 \times 10^{-23} / 6.628 \times 10^{-34} + \Delta S^*/8.314$$

$$-7.255 = 23.75 + \Delta S^*/8.314$$

$$-7.255 - 23.762 = \Delta S^*/8.314$$

$$31.017 = \Delta S^*/8.314 = -257.87$$

$$\Delta S^* = -257 \text{ JK}^{-1}$$

The ΔG^* can be calculated using,

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

$$\Delta H^* = +5188.4, \Delta S^* = -257 \text{ JK}^{-1},$$

Temperature: At different temperature in Kelvin (298K, 313K and 323K)'.
 $\Delta G^*_{25} = +5188.4 - 298 \times (-257) = +5188.4 - (-298 \times 257) = 82250$
 $\Delta G^*_{25} = 82.25 \text{ kJK}^{-1}$

$$\Delta G^*_{40} = +5188.4 - 313 \times (-257)$$

$$= +5188.4 + 80441 = 85629.4$$

$$\Delta G^*_{40} = 85.629 \text{ kJK}^{-1}$$

$$\Delta G^*_{50} = +5188.4 - (323 \times -257)$$

$$= +5188.4 + 83011 = 88199.4$$

$$\Delta G^*_{50} = 88.199 \text{ kJK}^{-1}$$

Therefore the free energy of activation ΔG^* at 25°C, 40°C and 50°C are 82.25 kJK⁻¹, 85.629 kJK⁻¹ and 88.199 kJK⁻¹ respectively.

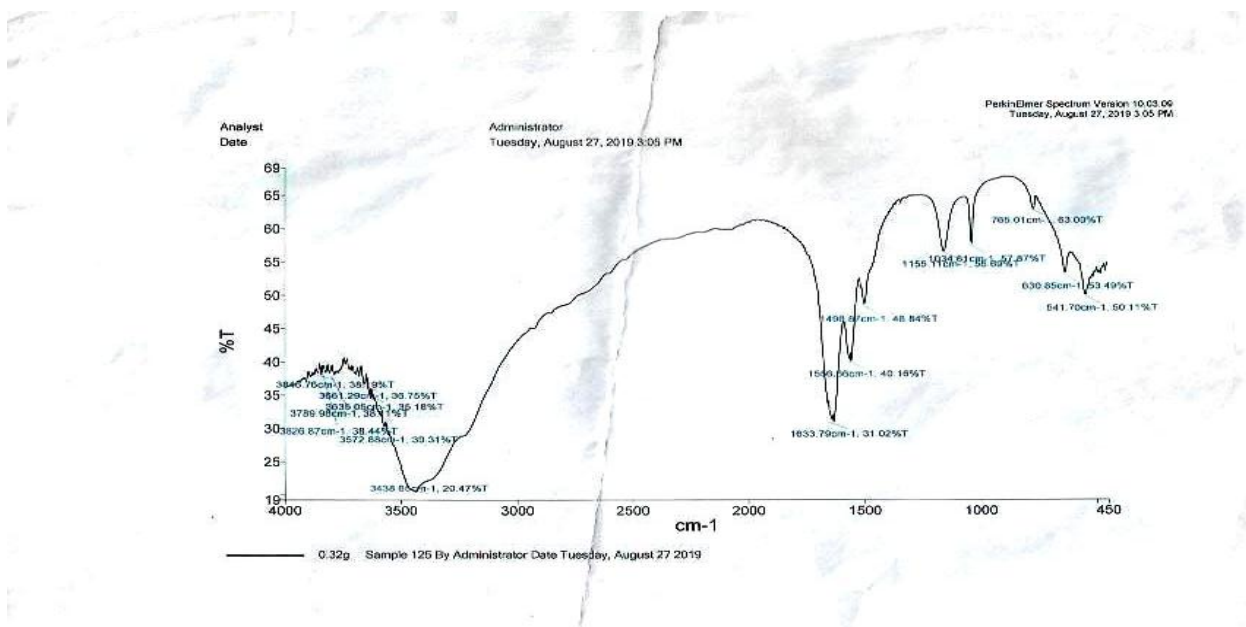


Figure-8: FT-IR of Hexakis (Urea) Chromium (III) Chloride.

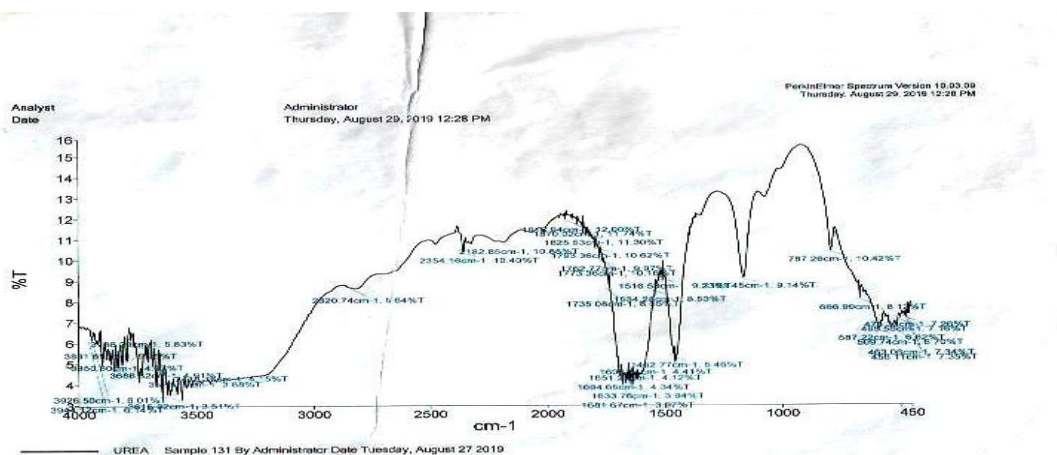


Figure-9: FT-IR spectrum of free urea.

Conclusion

From this study the equation of chromium hexaurea complex was ascertained to obey a first order kinetics. The average observed rate constant k_{obs} for the three different temperature 25°C, 40°C and 50°C are 2.5×10^{-2} , 3.04×10^{-2} and 3.3×10^{-2} respectively. The activation parameter obtained from the Eyring plot are enthalpy of activation $\Delta H^* = +5.19 \text{ kJ K}^{-1}$, the entropy of activation $\Delta S^* = -258 \text{ J K}^{-1}$ and $\Delta G^*_{25} = 82.25 \text{ kJ K}^{-1}$, $\Delta G^*_{40} = 85.62 \text{ kJ K}^{-1}$, $\Delta G^*_{50} = 88.199 \text{ kJ K}^{-1}$. The negative value of the entropy of activation ΔS^* suggests an associative mode of mechanism. The positive value of enthalpy suggest the reaction is endothermic reaction.

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