KINETICS OF CO (II), Ni (II) AND Cu (II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE –DL ALANINE

G. INDIRA DEVI

Associate Professor, Z. G. College, Kozhikode, Kerala, India

ABSTRACT

Thermal studies of cobalt, nickel and copper complexes of anthracene carboxaldehyde –DL- Alanine have been carried out. The kinetic parameters like the change in entropy, Arrhenius factor and activation energy of the decomposition of complexes were determined. Their decomposition mechanism and order of decomposition reaction were calculated. Anthracene Carboxaldehyde Alanine synthesized is a bidentate ligand. All complexes are colored and are soluble in hot methanol and ethanol. Co (II), Ni (II), and Cu (II) complexes synthesized, assigned the general formula $[ML_2 (H_2O)_2]$. Using Mechanistic equation, it is observed that, the cobalt and copper complexes have cylindrical symmetry and spherical symmetry for nickel complex, Order of decomposition for cobalt complex is $1/2$, for nickel complex it is $2/3$ and for copper it is $1/3$.

KEYWORDS: Arrhenius Factor, Entropy of Activation, Parameters, Bidentate & Thermal Decomposition

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INTRODUCTION

In 1798, Tassart¹ prepared orange colored crystals having the composition, $CoCl_3 \cdot 6NH_3$ by the reaction between $CoCl_3 \cdot 6H_2O$, and ammonia. This experimental observation was a puzzle in coordination chemistry. Schiff bases are ketimines or aldimines which are formed by the bonding between nitrogen atom of amine and carbon of aldehyde or ketonic group. Hence schiff base possesses azo methine group $>C=N$. A detailed study of Schiff base complexes were carried out in recent years.^{2,3} Pfeiffer et al⁴⁻⁸ reported a detailed study of Schiff bases. The methods of preparation of Schiff bases and the thermal analysis of the complexes copper, zinc and nickel obtained from alanine and vanillin were reported by Li, Shu - Lan and coworkers^{9,11,12}. Different metal complexes possess different solubility and stability. The use of amino acid Schiff base complexes as analytical reagents for quantitative estimation of metals were carried out^{13,14}. According to Mukerjee¹⁵ the Salicylaldehyde – glycine schiff bases can be used as colorimetric reagent. Ray¹⁶ reported the preparation, characterization and thermogravimetric analysis of iron complexes of tridentate di basic salicylidene / substituted salicylidene amino acids. The manganese Schiff base complexes derived from salicylaldehyde and alanine was reported by Chandra et al¹⁷.

EXPERIMENTAL

The anthracene carboxaldehyde and DL-alanine in aqueous alcohol were refluxed and metal salt solution was added and refluxed again. Complexes were separated by concentrating this solution by evaporation and cooling. The complexes thus formed were washed, dried and the yield noted. The complexes and ligand were characterized by micro analytical methods, magnetic studies, UV and IR studies and measurements of conductance. They were subjected to thermal studies at the heating rate of 10^0 centigrade per minute. Mechanistic

and non mechanistic equations were used for the calculations.

RESULTS AND DISCUSSIONS

The ligand Anthracene carboxaldehyde –DL alanine synthesized was found to be soluble in aqueous alcohol. The structure for the ligand assigned in this study is given below.

Ligand anthracene carboxaldehyde alanine	Carbon	Hydrogen	Nitrogen
Elemental data found–	77.2	4.88	5.5
Calculated data for C ₁₈ H ₁₅ NO ₂	77.92	5.41	5.05

The complexes synthesized are found to be colored. A general formula [ML₂ (H₂O)₂] was assigned to the synthesized complexes. The micro analytical data, molar conductivity and Magnetic measurement values are tabulated in Table 1.

Molar conductance measurements of these complexes in aqueous methanol were carried out which proved that they are non-electrolytes.

The magnetic moment values of Cu (II) complex were found to be 1.85 BM and so an octahedral geometry was assigned to this complex. Magnetic moment values of 2.82 BM and 4.93 BM were observed for Ni (II) and Co (II) complexes respectively, and they are also possessing octahedral structure.

A comparison of IR spectra of the complexes and ligands were carried out. A band of 1659 cm⁻¹ with medium intensity is observed. It is because of the carbonyl stretching frequency of the carboxylate group. Metal bonded to ligand carbonyl oxygen is suggested from the observed shift in frequencies in the spectra of complexes. Another region of the range 1700 – 1500 cm⁻¹ showed a shift because of complexation of ligand with metal. Schiff bases have C = N in the range 1690 – 1470 cm⁻¹ and a band occurred at 1553 cm⁻¹ in ligand and in complexes, the band occurred was at 1510 – 1546 cm⁻¹, which indicates the participation of azomethine nitrogen in coordination.

The effect of the frequencies in the I R spectra is not predictable due to the presence of two carboxylate groups in the complexes. The stretching vibrations of the carboxylate groups were 1650 to 1670 cm⁻¹ and 1440 to 1493 cm⁻¹, which are the asymmetric and symmetric vibrations. There was a change in frequency value of about 150 cm⁻¹ which indicates the monodentate behavior of carboxylate groups. M – O and M – N in the region ≈ 426 cm⁻¹ and ≈ 598 cm⁻¹ respectively were observed, which is due to the bonding of oxygen and nitrogen in the metal complexes. A broad band at 3500 – 3000

cm⁻¹ indicates the presence of coordinated water.

In the electronic spectra of ligand two bands at 24096 cm⁻¹ and 32467 cm⁻¹ are observed, which shows a red shift. This is an indication of the presence of Schiff base in coordination. Two bands 10530 cm⁻¹ and 23954 cm⁻¹ of the electronic spectra of cobalt complex is due to the shift of ⁴T_{1g}(F) to ⁴T_{2g}(F) and ⁴T_{1g}(F) to ⁴T_{1g}(P) transitions. The similar property is shown by nickel complex, with two bands, one at 10110 cm⁻¹ and the other at 22560 cm⁻¹. The copper complex is having absorption band at 16155 cm⁻¹. Hence the three complexes of anthracene carboxaldehyde alanine with cobalt, copper and nickel are having octahedral geometry.

Non isothermal studies with a heating rate of 10⁰ per minute was carried out for the Co(II), Ni(II), and Cu(II) complexes of anthracene carboxaldehyde alanine. The mass losses are determined for each stage and they are found to be in agreement with their 1:2 stoichiometry.

Table 1: Micro Analytical Data of Transition Metal Complexes of Anthracene Carboxaldehyde Alanine

Metal Complexes	Color	Melting Point	M%	C%	H%	N%	μ _{eff} BM	Ω _m ⁻¹
[CoL ₂ (H ₂ O) ₂]	Yellow	160	9.3(10.1)	66.98 (66.73)	4.83(4.94)	4.4(4.33)	4.93	4.64
[NiL ₂ (H ₂ O) ₂]	Orange	122	9.24 (9.1)	66.71 (66.76)	4.82(4.94)	4.4(4.33)	2.82	9.4
[CuL ₂ (H ₂ O) ₂]	Green	118	9.75(9.74)	66.26 (66.27)	4.91(4.91)	4.29(4.3)	1.85	6.5

Calculated values are give in paranthesis, M - Metal, Ω_m⁻¹ – Molar conductance in ohm⁻¹ cm² mol⁻¹

The instrumental T G Curves of cobalt anthracene carboxaldehyde alanine was drawn as mass Vs temperature, and is given in figure below

Figure 1

Table 2: Thermal Decomposition Data

Complex	Stage	Temp Range in TG (C)	Peak Temp in TG (C)	Loss of Mass Percentage			
				From TG	Theoretical	Pyrolysis	
[CoL ₂ (H ₂ O) ₂]	I	110 - 390	280	89.1	88.42		loss of 2 H ₂ O + 2L Co L ₂ (H ₂ O) ₂ ---> Co ₃ O ₄
				89.1	88.42	87.16	
[NiL ₂ (H ₂ O) ₂]	I	120 - 440	250	77.1	77.63		loss of 2 H ₂ O + L + ACA part loss of alanine part Ni L ₂ (H ₂ O) ₂ --> Ni O
	II	440 - 590	510	11.5	10.82		
				88.6	88.45	88.24	
[CuL ₂ (H ₂ O) ₂]	I	130 - 310	260	61.17	63.84		loss of 2 H ₂ O + 2 ACA loss of alanine part Cu L ₂ (H ₂ O) ₂ ---> Cu O
	II	310 - 490	470	13.39	13.19		
	III	490 - 620	600	12.37	10.75		
				87.79	86.93	87.8	

The pyrolytic experimental data, total mass loss, the temperature ranges etc are presented in Table 2. The kinetic parameters calculated using nine mechanistic equations are summarized in Table 3, which include the kinetic parameters evaluated. The suggested mechanism of decomposition and order of reaction were also calculated.

Table 3: Calculations using Mechanistic Equations

Parameter	Mechanistic Equations								
	1	2	3	4	5	6	7	8	9
E	31.73	34.48	38.51	35.82	18.61	18.61	18.61	17.31	17.93
A	1.22x10 ¹²	1.19 x10 ¹³	1.99 x10 ¹⁴	1.13 x10 ¹³	7.84 x10 ⁶	3.92 x10 ⁶	2.61 x10 ⁶	8.81 x10 ⁵	1.19 x10 ⁶
ΔS	-50.21	-45.68	-40.09	-45.79	-73.97	-75.35	-76.15	-78.31	-77.70
r	0.9968	0.9985	0.9989	0.9991	0.9981	0.9981	0.9981	0.9985	0.9984
E	23.55	27.62	27.33	26.00	13.74	13.74	13.74	12.19	12.69
A	5.77 x10 ⁶	2.28 x10 ¹⁰	4.70 x10 ⁹	1.03 x10 ⁹	7.03 x10 ⁴	3.52 x10 ⁴	2.35 x10 ⁴	5.71 x10 ³	6.84 x10 ⁴
ΔS	-65.32	-58.01	-61.15	-64.16	-83.22	-84.60	-85.41	-88.22	-87.85
r	0.9976	0.9980	0.9930	0.9950	0.9884	0.9884	0.9884	0.9937	0.9921
E	33.54	37.22	38.36	39.16	14.58	16.21	18.06	17.07	15.30
A	1.15 x10 ¹³	3.22 x10 ¹⁴	2.59 x10 ¹⁴	6.08 x10 ¹⁴	1.04 x10 ⁵	3.20 x10 ⁵	1.69 x10 ⁶	8.07 x10 ⁵	8.20 x10 ⁴
ΔS	-45.69	-39.06	-39.49	-37.80	-82.48	-80.21	-76.94	-78.41	-82.95
r	0.9951	0.9968	0.9971	0.9977	0.9923	0.9926	0.9959	0.9945	0.9947

In the case of these metal complexes a loss of mass is noted at around 150 °C, which is due to the loss of two coordinated water molecules. Due to the loss of two molecules of water and two ligand part, a single stage decomposition pattern is obtained for the cobalt complex. A double stage pattern of decomposition is obtained for nickel complex and in the first stage of this, two-coordinated water molecules and an anthracene carboxaldehyde part are lost and in the second stage removal of alanine part is occurred. For copper complex, a three stage decomposition pattern is obtained. The loss of two anthracene carboxaldehyde part of the ligand and two molecules of water is the first stage, loss of an alanine part contributes the second stage and for third stage, loss of another alanine part. In the final stage, the mass loss obtained is in agreement with that of the conversion of complexes to respective oxides, namely Co₃O₄, NiO and CuO.

The thermal stability of metal chelates can be determined from the initial decomposition temperature. The thermal stability of these chelates can be assigned as [Co L₂ (H₂O)₂] > [Cu L₂ (H₂O)₂] > [Ni L₂ (H₂O)₂], based on experimental

results.

The value of correlation coefficient, ($r \approx 1$), obtained are in good agreement with experimental data. The change in entropy values of these complexes are negative indicate that the decomposition reactions are slower and the molecules of complexes are more ordered.

The results show that a good linear curve with a high value of correlation coefficient is obtained for more than one equation and also found that the activation energy for decomposition increases with the thermal stability of the complex.

The kinetic parameters were calculated for the decomposition of cobalt complex using non mechanistic equation with an order of $1/2$, is in good agreement with those obtained for the R_2 mechanism based on phase boundary reaction cylindrical symmetry. In the case of nickel complex, R_3 mechanism is suggested based on phase boundary reaction spherical symmetry with order $2/3$. For copper complex, the order $1/3$ gives maximum correlation and hence R_2 mechanism is suggested.

From these studies, we conclude that the colored complexes of copper, nickel and cobalt of anthracene carboxaldehyde alanine possess octahedral structure and are thermally stable.

CONCLUSIONS

The thermo gravimetric analysis of the anthracene carboxaldehyde alanine complexes of copper, nickel and cobalt, were executed at the heating rate of 10^0 C per minute in static air. From the results of this study, it is concluded that they possess octahedral geometry with order of decomposition $1/3$, $2/3$ and $1/2$ respectively. It is also found that they are thermally stable.

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