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Study of Activation Energy and Thermodynamic Parameters from TGA of Some Synthesized Metal Complexes

KEYWORDS: Schiff base, Metal complexes, thermal degradation, activation parameters

K. R. Patel	Dhara Patel	Ashish patel
General Department, M. L. Institute of Diploma Studies, At & Post-Bhandu, Mehsana-Unjha Highway, Ta- Visnagar, Dist-Mehsana. Pin-384120.	General Department, M. L. Institute of Diploma Studies, At & Post-Bhandu, Mehsana-Unjha Highway, Ta- Visnagar, Dist-Mehsana. Pin-384120.	General Department, M. L. Institute of Diploma Studies, At & Post-Bhandu, Mehsana-Unjha Highway, Ta- Visnagar, Dist-Mehsana. Pin-384120.

ABSTRACT *Transition Metal complexes of Co(II),Cu(II) and Ni(II) with Schiff base have been synthesized . They were characterized by Elemental analysis, Infrared spectra, Electronic spectra and Thermo gravimetric analysis studies. Kinetic Parameters, such as energy of activation (Ea), enthalpy (ΔH#), entropy (ΔS#) and Gibbs energy (ΔG#), were computed from the TGA data. Based on the thermal studies, Thermal stability and kinetic parameters of these complexes were studied by employing Thermo gravimetric Analysis (TGA). The TGA graph shows that the complexes are stable up to 300 °C temperature. Decomposition takes place in four stages. Activation energy for decomposition has been calculated using Broido method. Mathematical analysis of the data has allowed us to determine various parameters using integral method using the coats-Redfern equation and the approximation method using the Horowitz-Metzger equation. The trend of the kinetic parameters was found to be different from that of the thermal stability order.*

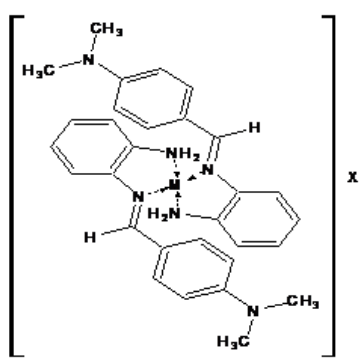
INTRODUCTION

The metal complexes of Schiff bases derived from heterocyclic compounds have been the centre of attraction for many workers in recent years.[1-3]. The physico-chemical data suggested tetrahedral geometry for the Cu(II), Co(II) and Ni(II) complexes. Thermo kinetic and spectral studies of metal complexes some Schiff bases [4] TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, In presence study The thermal behaviour (TGA) of the complexes was studied and kinetic parameters were determined by Broido method [5]. Very few systems have been reported [6] showing the relationship between thermal stability of metal chelates and structure of the chelating agents. Wendlandt and co-workers[7-9] and Hill and co-workers[10] studied the thermal properties of metal chelates with different types of complexing ligands. Structural studies on several metal chelates of 1-diketones and 2-hydroxycarbonyl compounds have been reviewed by Holm and O' Connor. The Broido method was used to evaluate the kinetic parameters from the TGA curves. Plots of ln(ln 1/y) versus 1000/T (where y is the fraction not yet decomposed) for different stage of the thermal degradation of the complexes and evaluation of kinetic parameters the integral method using the Coats-Redfern equation and the approximation method using the Horowitz- Metzger equation.

EXPERIMENTAL

Synthesis of Co(II), Cu(II) and Ni(II) complexes

The complexes were prepared by mixing Schiff base (0.1mol) in hot ethanol solution to (0.1mol) metal chloride salt solution prepared in distilled water. The schiff base solution was added slowly with continuous stirring to metal solution. It was refluxed for 3 hours and after refluxation, the mixture was heated for 10 minutes till the contents was reduced to half. Then the crystals precipitated out after being cooled. The precipitate was filtered and washed with the distilled water. All crystals were dried and kept in vacuum desiccators.



Where M =Co(II) or Ni(II) or cu(II)
and
X = 6 H2O. Cl2 or 4 H2O. Cl2 or 2 H2O.Cl2

Elemental analyses were performed with a Perkin-Elmer 2400 series –II, C-H-O-N-S analyzer. The metal content was determined [11] by titration with a solution of standardized disodium salt of EDTA after. The conductivity of complexes was measured in DMF as solvent using conductivity meter model, Systronic 361 μ digital. All the complexes showed the molar conductance values for 10-3M concentration in range 2 to 78 $ohm^{-1}cm^2$ mol^{-1}. The IR spectra were recorded in the range 4000–400 cm-1 on a Perkin-Elmer-783 instrument in KBr pellets. Thermo gravimetric analysis of the metal complexes was carried out in air by heating at a constant rate of 10°C per minute using a Perkin-Elmer TGA-7DSC-PYRIS-1-DTA-7 thermal analysis system. The activation energy (Ea) of the degradation process were obtained by the Broido method

RESULTS AND DISCUSSION

All the synthesized metal complexes in DMF. The analytical data were summarized in [Table1] reveals a stoichiometry of 1:2, metal: ligand. The molar conductance values of 10^{-3} M solutions in DMF were in the range of 8.58–16.22 $ohm^{-1}cm^2$ mol^{-1}, indicating a non-electrolytic behavior of the complexes.

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Infrared & Electronic Spectra

IR and Electronic spectral data were summarized in [Table2]. The band similar in behavior to $–NH_2$ stretching of Schiff base studied complexes is observed in all complexes; but it has shifted to ~3382 cm^{-1} for Ni(II),~ 3411 cm^{-1} for Co(II) and ~3388 cm^{-1} for Cu(II) respectively. This shift again accounts for coordination of –NH group of Schiff base with metal ions. Two bands which are strong and are of medium intensity in range of 511-640 cm^{-1} and 685-750 cm^{-1} in studied complexes. These can be M-N and M-N=C stretching respectively. A sharp and strong band obtained ~746 cm^{-1} in complexes can be attributed to M-NH stretching. Sharp and medium intensity bands are observed at ~1676 cm^{-1} in IR spectra of all complexes which represent M-OH2 stretching.

The complex of Ni(II) has shown electronic transitions at 5154 cm-1 (υ1), 11494 cm^{-1} (υ2) and 13333 cm^{-1} (υ3) respectively. The value 5154 cm^{-1} at which the first transitions occur is too high for a tetrahedral complex. The complex of Co(II) has shown electronic transitions at 4237 cm-1 (υ1), 5208 cm^{-1} (υ2) and 11494 cm^{-1} (υ3).The value 4237 cm^{-1} at which the first transitions occur is too high for a tetrahedral complex. The dark green colored complex of Cu(II) has shown electronic transitions bands between 11764 cm^{-1} -26315 cm^{-1} broad band suggested for tetrahedral geometry.

Thermal studies

The cumulative weight loses of metal complexes at 50C, 100°C, 150°C, 200°C and 250°C are presented in [Table 3] Decomposition of all complexes starts above 350oC. The rate of decomposition of metal complexes is lower than that of the ligand suggested that there may be weak intermolecular hydrogen bonding. Co(II) thermograms also shows the presence of six water molecules and loss in weight equivalent to 15-20% at 100°C to 150°C. Again presence of water molecules is observed in Cu(II) complexes. These complexes show loss 5 to 8% equivalent to two water molecules at 100°C to 150°C.The final product is found to be metal oxide in all the complexes. Thermo gravimetric analysis shows that all synthesized complexes are hydrated and have water molecules associated to them. Co(II) has six, Ni(II) has four and Cu(II) has two water molecules as part of their structure. All complexes lost hydration water 50°C and 150°C and then the co-ordinated water molecule was lost above ≥250°C.The decomposition was complete at >600°C for all complexes. The TGA curves of all complexes were shown in [Figure 1].

Activation Energy and Thermodynamic Parameters studies

The Broido method was used to evaluate the kinetic parameters from the TGAcurves. Plots of ln(ln 1/y) versus 1000/T (where y is the fraction not yet decomposed) for four stage of the thermal degradation of the complexes are shown in [Figure2] . The slope of the plot ln(ln 1/y) versus 1000/T is related to the energy of activation as

$$Ea = –2.303 \times R \times slope \quad (1)$$

Where, R = gas constant.

The parameters, enthalpy (DH#), entropy (DS#) and Gibbs energy (DG#) of activation were calculated using the following standard equations

$$DH\# = Ea – R\,Td \quad (2)$$

$$DS\# = DH\#/T – 4.576 \log T/K' – 47.22 \quad (3)$$

where $K' = –ln(ln\ 1/y)$

$$DG\# = DH\# – DTS\# \quad (4)$$

The activation energies of decomposition were the range (15.41-98.57), (15.93-37.55),and (17.34-67.65) kJ mol-1 in Cu(II), Co(II) and Ni(II) respectively. The high values of the activation energies reflect the thermal stability of the complexes[12-13]. The entropy of activation (DS#) and enthalpies of activation(DH#) values for four steps of all the complexes are negative and the negative values of the entropies of activation are compensated by the values of the enthalpies of activation leading to almost the same values (27827-28731 kJ mol^{-1}) for the free energies of activation(DG#). The data were summarized in [Table 4]. The entropy of activation had negative values in all the complexes, which indicates that the decomposition reactions proceed with a lower rate than normal ones.

Kinetic calculations

The kinetic and thermodynamic parameters viz. the order of the reaction (n), the energy of activation (Ea), the pre-exponential factor (Z), the entropy of activation (ΔS#) and the Gibbs energy change (ΔG#), together with the correlation coefficient (r) for the non-isothermal decomposition of the metal complexes, were determined by the Horowitz–Metzer (HM) approximation method[14] and the Coats–Redfern integral method. The obtained data are given in [Table 5]. The results showed that the values obtained by two methods are comparable. The calculated values of the activation energy of the complexes are relatively low, indicating the autocatalytic effect of the metal ion on the thermal decomposition of the complex. The negative activation entropy value indicates that the activated complexes were more ordered than the reactant and that the reactions were slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer electronic transitions.

Table – 1 Analytical Data of the Metal Complexes

Crystals	Molecular Formula	Colour	Formula weight	Yield %(g)	Analysis of elements (%) found (calculated)						Molar Conductance Ohm-1 cm2 Mol-1	D.P. (0C)
					M	C	H	N	O	Cl		
[Co·L2] ·6H2O·Cl2	CoC30H4 6N6O6Cl2	Green	714.933	63 (6.02)	8.24 (8.11)	50.4 (50.38)	6.43 (6.39)	11.74 (11.68)	13.41 (13.37)	9.93 (9.85)	8.58	>600
[Ni·L2] ·4H2O·Cl2	NiC30H4 2N6O4Cl2	Brown	678.699	61 (5.49)	8.64 (8.59)	53.09 (52.96)	6.18 (6.10)	12.37 (12.33)	9.42 (9.38)	10.46 (10.41)	16.22	>600
[Cu·L2] ·2H2O·Cl2	CuC30H3 8N6O2Cl2	Brown	647.546	65 (5.80)	9.81 (9.77)	55.64 (55.56)	5.86 (5.83)	12.97 (12.91)	4.93 (4.88)	10.96 (10.90)	8.74	>600

Table – 2 Infrared and Electronic spectral data of Metal Complexes

Crystal	Infrared Spectral Analysis									Electronic Spectra Analysis			
	υ-N-CH3 Schiff base	υ-C=C- Schiff base	υ-C=NH Schiff base	υ-C-H Schiff base	υ –CH2 Schiff base	υ-C-N Schiff base	υ-M-OH2 Metal	υ M-N Metal	υ M-N=C Metal	Absorption region (cm-1)	Band assignment	Magnetic moment μeff (B.M.)	Geometry
[Co·L2] ·6H2O·Cl2	1515 (s)	2920 (m)	3411 (b)	2810 (m)	1368 (b)	1248 (s)	1609 (s)	640 (m)	750 (s)	5208 cm-1 11764 cm-1 18867 cm-1	4A2 à 4T2 4A2à 4T1 4A2à 4T1 (p)	1.73	Tetrahedral
[Ni·L2] ·4H2O Cl2	1519 (s)	-	3382 (b)	-	1374 (b)	1217 (s)	1607 (s)	633 (m)	746 (m)	5154 cm-1 11494 cm-1 13333 cm-1	3T1 à 3T2 3T1 à 3A2 3T1 à 3T1	2.83	Tetrahedral

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[Cu·L2] ·2H2O·Cl2	1519 (s)	3040 (m)	3338 (b)	2941 (m)	1372 (b)	1215 (m) 1167 (s)	1676 (s)	511 (b)	746 (s)	11764 cm-1 26315 cm-1 Broad band	T1----4T2 3T2----4T2	1.73	Tetrahedral

Table – 3 Thermogravitomatric Analyses of some Metal Complexes

Crystal	Found									
	50oC		100oC		150oC		200oC		250oC	
	G	%	G	%	G	%	G	%	G	%
[Co·L2].6H2O·Cl2	7.14	1	107.23	15	142.98	20	150	24	193.00	27
[Ni·L2].4H2O.Cl2	0.678	0.1	61.08	9	101.80	15	122.16	18	156.1	23
[Cu·L2].2H2O·Cl2	0.64	0.1	32.37	5	51.80	8	77.70	12	116.55	18

Table -4 Activation energy and Thermodynamic parameters some metal complexes

complexes	stage	Temp range oC	Ea kJ mol-1	(H#)	(S#)	(G#)
[Co·L2] 6H2O Cl2	i	60-90	67.65324	-6608.49	-42.0776	27887.45
	ii	90-270	17.34607	-6658.8	-42.1534	27937.68
	iii	270-500	25.53418	-6650.61	-42.1411	27929.51
	iv	500-620	55.66773	-6620.47	-42.0956	27899.42
[Ni·L2] ·4H2O Cl2	i	60-130	30.86655	-6645.28	-42.0595	28716.94
	ii	130-220	15.93904	-6660.2	-42.0814	28731.84
	iii	220-490	37.55796	-6638.58	-42.0497	28710.25
	iv	490-640	20.33129	-6655.81	-42.075	28727.46
[Cu·L2] ·2H2O·Cl2	i	60-100	48.44321	-5879.44	-41.4362	27877.8
	ii	100-130	98.57009	-5829.31	-41.3617	27827.75
	iii	130-370	40.5706	-5887.31	-41.4479	27885.66
	iv	370-640	15.41761	-5912.46	-41.4852	27910.78

Table -5 The kinetic parameter of degradation of the metal complexes calculated by the Horowitz–Metzger and Coats–Redfern methods

complexes	stage	n	Method	Ea kJ mol-1	Z s-1	ΔS# J K-1 mol-1	ΔG# kJ mol-1	r
[Co·L2] 6H2O Cl2	I	1.10	Horowitz- Metzger equation	25.5320	0.7060	-47.2231	31299.00	0.95
	II			25.5012	0.9091	-46.3342	30709.66	0.95
	I	0.90	Coats- Redfern equation	58.7502	5.202	-43.0250	28515.66	0.95
	II			58.7451	5.313	-43.2201	28645.01	0.95
[Ni·L2] ·4H2O Cl2	I	0.80	Horowitz- Metzger equation	35.8632	9.41 X 1011	-48.0212	31828.14	0.96
	II			33.5574	3.5 X 109	-48.335	32036.19	0.96
	I	1.05	Coats- Redfern equation	19.2023	60.3	-55.809	37011.30	0.95
	II			16.2455	49.11	-55.707	36943.50	0.95
[Cu·L2] ·2H2O·Cl2	I	1.00	Horowitz- Metzger equation	101.2587	1.5 X 1027	-41.2281	27324.31	0.96
	II			99.5684	1.6 X 1023	-40.2323	26664.10	0.96
	I	1.42	Coats- Redfern equation	41.7862	1.9 X 106	-40.2051	26646.06	0.95
	II			40.5834	5.4 X 105	-40.1520	26610.86	0.95

Figure 1: TGA curves for metal complexes Fig 2: Plot of ln[ln(1/y)] vs 1000/T for metal (II) Complexes

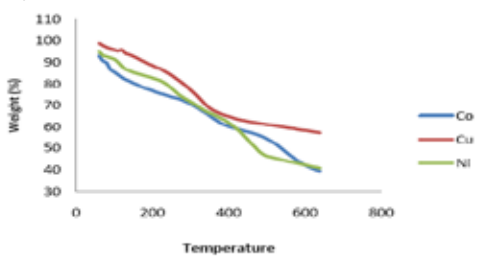
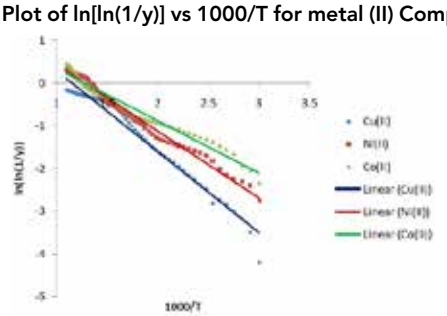


Fig 2: Plot of ln[ln(1/y)] vs 1000/T for metal (II) Complexes



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