Kinetics and Mechanism of the Thermal Decomposition of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Vanillin-2-aminopyridine

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The thermal decomposition of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates of vanillin-2-amino pyridine was studied by TG. The mechanism of the decomposition has been established from TG data. The kinetic parameters, *viz.*, activation energy E, pre-exponential factor A and order of reaction n, were calculated from the TG curves using mechanistic and non-mechanistic (Coats-Redfern) integral equations.

INTRODUCTION

Very few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating reagents[1]. Wendlandt[2–5] and Hill[6, 7] studied the thermal properties of metal chelates with different types of complexing ligands. Such studies on thermal decomposition and kinetics of metal chelates with azomethine ligands have been done by a few workers[8–11]. In continuation of our work[12–14] on thermal decomposition kinetics of metal chelates, we report in this paper the preparation, characterisation and thermoanalytical data of five transition metal complexes of a novel Schiff base, vanillin-2-amino pyridine. Nonisothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids[15–17]. This study therefore attempts to establish the mechanism of decomposition of $[MnLHCl(H_2O)_4]Cl$ and $[MLH(OAc)_2(H_2O)_3]$, where LH = vanillin 2-aminopyridine (VAAP) and $M = Co(II)$, Ni(II), Cu(II) or Zn(II).

EXPERIMENTAL

The ligand was prepared from vanillin and 2-aminopyridine following the reported procedure by Schiff. Mn(II) complex was prepared by mixing methanolic solution of the metal chloride with a solution of the ligand in methanol. The mixture was refluxed for 3 h and the separated complex was filtered, washed and dried in a vacuum desiccator over anhydrous $CaCl_2$. Co(II), Ni(II), Cu(II) and Zn(II) chelates of vanillin-2-aminopyridine were prepared by adding metal acetate in methanol to the boiling solution of the ligand until the metal to ligand ratio reached 1 : 2. Refluxed for 8 h and the resulting solution was added dropwise to distilled water with constant stirring. The product separated was collected, washed and dried.

The purity of the samples was checked by elemental analysis for the metal and C, H, N analysis. The structure of Mn(II) chelate was found to be [Mn(LH)Cl(H$_2$O)$_4$]Cl whereas the rest of the complexes were represented as [M(LH)(OAc)$_2$(H$_2$O)$_3$] where M = Co(II), Ni(II), Cu(II) and Zn(II) (Fig. 1 and
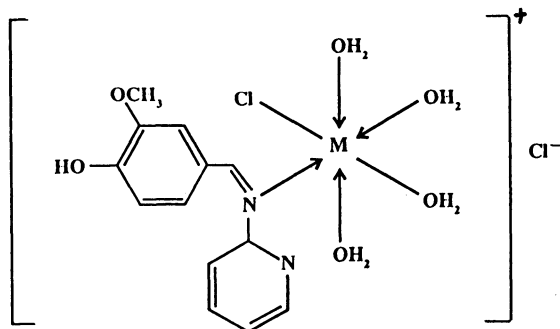
Fig. 1.
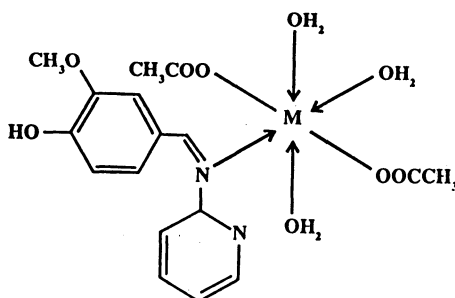
Fig. 2.   M = Co(II), Ni(II), Cu(II) or Zn(II)

2).

The IR spectra were recorded using Shimadzu FTIR-8101 spectrophotometer. Thermal analysis were carried out using a Perkin-Elmer-7 series thermal analysis system. A constant heating rate of 10°C min^{-1} and sample mass of *ca.* 5 mg were employed for the entire study. The atmosphere was static air. The fractional decomposition, α, was determined directly from TG curves; computational work was done with a Horizone-III minicomputer using the programming language FORTRAN.

The complexes were characterised on the basis of elemental analysis, spectral and thermal studies. A strong intense band due to v(C=N) stretch (azomethine) in ligand appears around 1674 cm^{-1} which upon complexation shifts towards lower wave member region indicating the participation of the azomethine nitrogen in coordination with metal ions. The appearance of the ligand v(O—H) vibration band suggests the coordination of a neutral ligand. Since the pyridine ring

deformation vibrations do not experience any positive or negative deviation, the non-involvement of pyridyl-N in complexation is inferred.

The presence of coordinated water molecules in all the present complexes is shown by the appearance of a broad and strong band at 3850–3250 cm^{-1} followed by a sharp peak at 840 cm^{-1}. Chelates of Co(II), Ni(II), Cu(II) and Zn(II) suggest the presence of a coordinated acetate group. The frequency difference value of about 200 cm^{-1} between these asymmetric and symmetric modes of acetate group further indicates unidentate nature of this group. On the basis of electronic spectral data and magnetic moment studies, one can assign octahedral structures for the complexes.

Mathematical Analysis of Data

The TG curves for Mn(II), Ni(II), Cu(II) and Zn(II) complexes exhibited a three stage decomposition pattern and that for Co(II) complex exhibited a four stage decomposition pattern. The first stage in all the above chelates represents the loss of water molecules above 150°C. According to Nikolaev et al.[18], water eliminated above 150°C can be considered as coordinated water. The second and third stage represent the major decomposition step. The mass loss consideration and X-ray diffraction data confirmed the products to be corresponding oxides.

Evaluation of the mechanism of reaction from non-isothermal methods has been discussed by Sestak and Berggren[19] and Satava[20]. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infintesimal time interval, that the rate can be expressed by an Arrhenius-type equation.

$$\frac{d(\alpha)}{dt} = Ae^{-E/RT}f(\alpha). \tag{1}$$

Where A is preexponential factor, t is the time and f(α) depends on the mechanism of the process. For a linear heating rate ϕ, $\frac{dT}{dt} = \phi$ and substitution into equation (1) gives

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} e^{-E/RT} dT \tag{2}$$

Integration of the left hand side of equation (2) gives

$$\int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = g(\alpha) = \int_0^T \frac{A}{\phi} e^{-E/RT} dT \tag{3}$$

where g(α) is the integrated form of f(α). A series of f(α) forms are proposed and the mechanism is obtained from that which gives the best representation of the experimental data. Nine probable reaction mechanisms given by Satava are given in Table-2. For evaluating kinetic parameters from the mechanistic equations, the right-hand side equation (3), the temperature integral, which is an incomplete gamma function, was used in the form given by Coats and Redfern[21] which is one of the best solutions recommended by several other authors[22, 23].

The general form of the equation used is

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\phi E} - \frac{E}{RT} \tag{4}$$

TABLE-1

THERMAL DECOMPOSITION DATA

Substance	Peak Temp. in TG (°C)	Temp. ranges in TG (°C)	Loss of Mass (%)			Probable assignments
			From T.G.	Theoretical	Pyrolysis	
$[Mn(LH)Cl(H_2O)_4]Cl$						
I stage	190	170–200	8.00	8.40		Loss of $2H_2O$
II Stage	320	260–320	40.00	40.40		Loss of $2H_2O$ + vanillin part
III Stage	450	390–490	32.00	33.20	81.00	Loss of aminopyridine part + 2Cl
$[Co(LH)(OAc)_2(H_2O)_3]$						
I Stage	160	110–200	10.00	11.80		Loss of $3H_2O$
II Stage	240	210–330	27.00	29.70		Loss of vanillin part
III Stage	338	330–340	24.00	20.10		Loss of aminopyridine part
IV Stage	350	340–400	22.00	21.20	83.10	Loss of 2 acetate
$[Ni(LH)(OAc)_2(H_2O)_3]$						
I Stage	150	120–300	41.00	41.50		Loss of $3H_2O$ + vanillin part
II Stage	302	300–310	29.00	26.50		Loss of aminopyridine part + 0.5 acetate
III Stage	340	310–390	15.50	16.00	84.98	Loss of 1.5 acetate
$[Cu(LH)(OAc)_2(H_2O)_3]$						
I Stage	120	90–120	8.00	7.70		Loss of $2H_2O$
II Stage	254	130–260	60.00	60.00		Loss of $1H_2O$ + L + 0.5 acetate
III Stage	300	260–400	14.00	15.60		Loss of 1.5 acetate
$[Zn(LH)(OAc)_2(H_2O)_3]$						
I Stage	180	130–200	11.00	11.60		Loss of $3H_2O$
II Stage	250	230–340	20.00	19.77		Loss of aminopyridine part
III Stage	420	340–450	50.50	51.14		Loss of vanillin part + 2 acetate

Along with the mechanistic equations non-mechanistic method suggested by Coats and Redfern[21] was also used for comparison. The reaction order can easily be eliminated by comparing the values using M = 0.33, 0.5, 0.66 and 1 in equations.

$$1 - (1 - \alpha)^{1-n}/(1 - n)T^2 \; vs. \; 1/T \quad \text{for} \quad n \neq 1 \tag{5}$$

$$\log(-\log(1 - \alpha)/T^2) \; vs. \; 1/T \quad \text{for} \quad n = 1 \tag{6}$$

$$\ln\left[\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2}\right] = \ln\left[\frac{AR}{\phi E}\frac{(1 - 2RT)}{E}\right] - \frac{E}{RT} \tag{7}$$

$$\ln\left[\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)}\right] = \ln\frac{ART_s^2}{\phi E} - \frac{E}{RTs} + \frac{EQ}{RTs^2} \tag{8}$$

RESULTS AND DISCUSSION

The decomposition temperature ranges of the metal chelates are given in Table-1. Data from independent pyrolytic experiments are also included in this table. The kinetic parameters calculated from TG for the nine mechanistic equations are given in Tables 3–5. The corresponding values of E, A and γ from non-mechanistic equation (Coats-Redfern) are given in Tables 6–8.

TABLE-2
KINETIC EQUATIONS

Function	Equation	Rate-Controlling Process
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1 - \alpha)\ln(-\alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D_3	$[1 - (1 - \alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion, spherical symmerty: Jander equation
D_4	$(1 - \tfrac{2}{3}\alpha) - (1 - \alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry: Ginstling-Brounshtein equation
F_1	$-\ln(1 - \alpha) = kt$	Random nucleation, 1 nucleus on each particle: Mampel equation
A_2	$-\ln(1 - \alpha)^{1/2} = kt$	Random nucleation: Avrami equation I
A_3	$-\ln(1 - \alpha)^{1/3} = k2$	Random nucleation: Avrami equation II
R_2	$1 - (1 - \alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$1 - (1 - \alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry

TABLE-3:
KINETIC PARAMETERS FOR DECOMPOSITION OF [Mn(LH)Cl(H₂O)₄]Cl & [Co(LH)(OAc)₂(H₂O)₃] FROM TG USING MECHANISTIC EQUATIONS

[Mn(LH)Cl(H₂O)₄]Cl										
I Stage	E	221.5080	223.0924	224.6672	168.5359	109.3396	109.2839	109.2889	108.1394	108.5380
	A	6.8824×10^{20}	5.3505×10^{20}	1.8352×10^{20}	7.1625×10^{13}	1.3356×10^{9}	6.5816×10^{8}	4.3935×10^{8}	4.7538×10^{8}	3.5439×10^{8}
	ΔS	−41.1132	−43.2075	−52.1077	−174.8450	−265.4217	−271.3080	−274.6698	−274.0143	−276.4572
	γ	0.9543	0.9547	0.9555	0.9783	0.9525	0.9527	0.9527	0.9518	0.9521
II Stage	E	25.5614	58.1017	69.4667	67.6767	31.4469	31.4636	31.4628	29.4569	30.1128
	A	4.7072×10^{-6}	4.7646×10^{1}	4.0373×10^{1}	2.5887×10^{1}	2.920×10^{-1}	1.4680×10^{-1}	9.7900×10^{-2}	8.5500×10^{-2}	6.8000×10^{-2}
	ΔS	−544.2817	−410.1175	−411.4951	−415.1913	−452.769	−458.2109	−461.5848	−462.7116	−464.6146
	γ	0.9474	0.9181	0.9356	0.9376	0.9163	0.9164	0.9164	0.9182	0.9176
III Stage	E	13.7217	23.7798	40.8001	29.1999	24.6183	24.6915	24.6166	10.3030	14.844
	A	3.6650×10^{-3}	2.6600×10^{-2}	3.090×10^{-1}	2.1680×10^{-2}	1.0990×10^{-1}	5.5800×10^{-2}	3.6600×10^{-2}	1.3474×10^{-3}	2.9109×10^{-3}
	ΔS	−490.5561	−474.0519	−453.7009	−475.7715	−462.2679	−467.9090	−471.4093	−493.9021	−492.4724
	γ	0.9928	0.9893	0.9803	0.9862	0.9593	0.9600	0.9593	0.9645	0.9637
[Co(LH)(OAc)₂(H₂O)₃]										
I Stage	E	130.1302	125.0773	131.9059	93.9795	62.8683	62.8666	62.8674	62.1948	62.4451
	A	1.8282×10^{11}	2.3764×10^{10}	3.5585×10^{10}	9.2245×10^{5}	1.3779×10^{4}	6.8872×10^{3}	4.5918×10^{3}	5.5346×10^{3}	3.9946×10^{3}
	ΔS	−223.9497	−439.6392	−237.5622	−325.3991	−360.3648	−366.1335	−369.5053	−367.9519	−370.6653
	γ	0.9348	0.9220	0.9363	0.9584	0.9300	0.9300	0.9300	0.9287	0.9291
II Stage	E	40.6929	44.1269	46.9351	45.3875	20.4147	20.5336	20.4147	18.2903	18.9848
	A	1.6707	2.1405	1.0539	6.6940×10^{-1}	4.0700×10^{-2}	2.1100×10^{-2}	1.300×10^{-2}	1.0400×10^{-2}	8.6729×10^{-3}
	ΔS	−436.7802	−434.7194	−440.6129	−444.3874	−467.6733	−473.1235	−476.8093	−506.1996	−480.5377
	γ	0.9443	0.9595	0.9629	0.9601	0.9491	0.9437	0.9491	0.9401	0.9433
III Stage	So rapid that could not be studied									
IV Stage	E	40.1605	60.7522	112.4837	76.4284	85.4664	85.4664	85.4664	38.0662	51.0516
	A	3.1515	1.9864×10^{2}	1.6822	1.3647×10^{3}	1.1355×10^{5}	5.6768×10^{4}	3.7844×10^{4}	1.7673	2.2084×10^{1}
	ΔS	−433.1175	−398.6529	−438.3391	−382.6234	−345.8498	−351.6148	−354.9879	−437.9289	−416.9235
	γ	0.9348	0.9955	0.9990	0.9991	0.9908	0.9908	0.9908	0.9998	0.9989

E in kJ mol⁻¹, A in s⁻¹, ΔS in J mol⁻¹ K⁻¹.

TABLE-4

KINETIC PARAMETERS FOR THE DECOMPOSITION OF [Ni(LH)(OAc)$_2$(H$_2$O)$_3$] AND [Cu(LH)(OAc)$_2$(H$_2$O)$_3$] FROM TG USING MECHANISTIC EQUATIONS

Substance	Para-meters	1	2	3	4	5	6	7	8	9
[Ni(LH)(OAc)$_2$(H$_2$O)$_3$]										
I Stage	E	55.7420	56.9145	59.6237	8.9246	26.8925	26.8934	26.8934	25.3518	29.4852
	A	1.6363×10^2	1.2355×10^2	6.145×10^1	5.899×10^2	3.8310×10^{-1}	1.9160×10^1	1.277×10^{-1}	1.155×10^{-1}	8.0200×10^{-2}
	ΔS	-397.0421	-399.3863	-405.2048	-386.3787	-477.4248	-453.1814	-486.6014	-457.4118	-460.4181
	γ	0.9435	0.9504	0.9528	0.9812	0.9426	0.9426	0.09426	0.9334	0.9362
II Stage	So rapid that could not be studied									
III Stage	E	6.4376	17.5109	44.7977	25.5258	34.7472	36.7480	36.7464	10.3377	17.2308
	A	9.8062×10^{-4}	1.9700×10^{-2}	4.8563	3.8800×10^{-2}	6.6770	3.3349	2.2254	2.9281×10^{-3}	1.5000×10^{-2}
	ΔS	-497.0636	-472.1172	-426.3010	-466.4786	-432.6525	-429.4158	-432.7914	-487.9645	-474.3621
	γ	0.8229	0.9390	0.9760	0.902	0.9753	0.9753	0.9753	0.9315	0.9605
[Cu(LH)(OAc)$_2$(H$_2$O)$_3$]										
I Stage	E	159.0040	159.7357	161.0706	174.4222	77.9090	77.8734	77.8742	77.1354	77.3933
	A	1.8027×10^{-17}	1.2101×10^{-17}	4.0144×10^{-16}	2.0010×10^{-18}	1.9095×10^{-7}	9.4327×10^{-6}	9.2908×10^{-6}	7.3152×10^{-6}	5.3244×10^{-6}
	ΔS	-108.3488	-111.6641	-120.8414	-88.3288	-299.3894	-305.2553	-308.6446	-307.3700	-310.0118
	γ	0.9627	0.9800	0.9674	0.7927	0.9595	0.9594	0.9594	0.9595	0.09595
II Stage	So rapid that could not be studied									
III Stage	E	4.0332	5.7440	19.6562	10.2390	14.7770	11.3091	-14.7762	1.3332	4.8909
	A	8.8260×10^{-5}	7.4559×10^{-4}	2.0100×10^{-2}	1.3581×10^{-4}	4.5333×10^{-2}	8.4443×10^{-3}	1.5109×10^{-2}	7.1332×10^{-5}	4.3558×10^{-4}
	ΔS	-519.6157	-501.8637	-474.3613	-499.9771	-467.7018	-481.6797	-476.8402	-521.3290	-506.3360
	γ	0.9753	0.9372	0.9905	0.9847	0.9716	0.9079	0.9716	0.8128	0.9674

E in kJ mol^{-1}, A in s^{-1}, ΔS in J mol^{-1} K^{-1}

TABLE-5

KINETIC PARAMETERS FOR THE DECOMPOSITION OF $[Zn(LH)(OAc)_2(H_2O)_3]$ FROM TG USING MECHANISTIC EQUATIONS

Substance	Parameters	1	2	3	4	5	6	7	8	9
$[Zn(LH)(OAc)_2(H_2O)_3]$										
I Stage	So rapid that could not be studied									
II Stage	E	61.7954	64.3839	68.1558	60.9712	31.4122	31.4004	28.0818	28.9269	29.7436
	A	7.0053×10^2	8.1573×10^2	4.4412×10^2	6.8787×10^1	1.6425	8.1880×10^{-1}	2.229×10^{-1}	3.3967×10^{-1}	3.757×10^{-1}
	ΔS	15.4763	16.7427	11.6856	-3.872	-34.8920	-40.6816	-51.5020	-6.6475	-48.0519
	γ	0.9760	0.9781	0.9791	0.9801	0.9742	.9742	0.9626	0.9717	0.9726
III Stage	E	32.9275	38.6661	45.4763	41.0098	20.9769	20.9769	20.9769	15.7218	17.4104
	A	3.9050×10^{-1}	8.28103×10^{-1}	9.7150×10^{-1}	3.2562×10^{-1}	7.3346×10^{-2}	3.6670×10^{-2}	2.4446×10^{-2}	8.6401×10^{-3}	9.2519×10^{-3}
	ΔS	-45.0355	-38.7829	-37.4532	-46.5211	-58.9443	-64.7101	-68.0828	-76.7336	-76.16647
	γ	0.9780	0.9807	0.9827	0.9809	0.9754	0.9754	0.9754	0.9673	0.9606

E in kJ mol^{-1}, A in s^{-1}, ΔS in J mol^{-1} K^{-1}

TABLE-6

KINETIC PARAMETERS FOR THE DECOMPOSITION OF [Mn(LH)Cl(H₂O)₄]Cl AND [Cu(LH)(OAc)₂(H₂O)₃] FROM TG USING MECHANISTIC EQUATIONS

Substance	Para-meters	From Coats-Redfern equation	From mechanistic equation	Reaction mechanism	Orders of reaction
[Mn(LH)Cl(H₂O)₄Cl]	E	109.3396	109.3396	Equation V	
I Stage	A	1.3356×10^9	1.3556×10^9	F_1 mechanism	
	ΔS	−265.4217	−265.4217	Random nucleation	1
	γ	0.9525	0.9525	Mampel equation	
II Stage	E	29.2300	31.4636	Equation V_1	
	A	1.4553×10^{-1}	1.4680×10^{-1}	A_2 mechanism	
	ΔS	−458.4059	−458.2109	Random nucleation	
	γ	0.9189	0.9164	Avrami equation 1	1/3
III Stage	E	14.4877	13.7217	Equation 1	
	A	4.3443×10^{-3}	3.6650×10^{-3}	D_1 mechanism	
	ΔS	−487.5058	−490.5563	One-dimensional diffusion	
	γ	0.9637	0.9928		2/3
[Co(LH)(OAc)₂(H₂O)₃]	E	61.3601	62:1948	Equation VIII	
I Stage	A	5.4165×10^3	5.5346×10^3	R_2 mechanism	
	ΔS	−368.1315	−367.9519	Phase boundary reaction	1/2
	γ	0.9246	0.9287	Cylindrical symmetry	
II Stage	E	20.2414	20.4741	Equation VII	
	A	1.3617×10^{-2}	1.3600×10^{-2}	A_3 mechanism	
	ΔS	−474.1838	−476.8093	Random nucleation	2/3
	γ	0.9401	0.9491	Avrami equation II	
III Stage		So rapid that could not be studied			
IV Stage	E	85.4697	85.4664	Equation VI	
	A	5.7842×10^4	5.6768×10^4	A_2 Mechanism	
	ΔS	−348.9638	−351.6148	Random Nucleation ·	1/2
	γ	0.9908	0.9908	Avrami Equation I	

E in kJ mol⁻¹, A in s⁻¹, ΔS in J mol⁻¹ K⁻¹

TABLE-7

KINETIC PARAMETERS FOR THE DECOMPOSITION OF [Ni(LH)(OAc)$_2$(H$_2$O)$_3$] AND
[Cu(LH)(OAc)$_2$(H$_2$O)$_3$] FROM TG USING COATS-REDFERN EQUATION AND
ACCEPTED MECHANISTIC EQUATIONS

Substance	Para-meters	From Coats-Redfern equation	From mechanitic equation	Reaction mechanism	Order of reaction
[Ni(LH)(OAc)$_2$(H$_2$O)$_3$]					
I Stage	E	25.2156	26.8934	Equation VI	
	A	1.900×10^{-1}	1.9160×10^{-1}	A$_2$ mechanism	
	ΔS	–453.2559	–453.1814	Random nucleation	1/3
	γ	0.9300	0.9426	Avramic equation I	
II Stage	So rapid that could not be studied				
III Stage	E	36.7472	36.7472	Equation V	
	A	6.6770	6.6770	F$_1$ mechanism	
	ΔS	–423.6525	–423.6525	Random nucleation	1
		0.9753		Mampel Equation	
[Cu(LH)(OAc)$_2$(H$_2$O)$_3$]					
I Stage	E	77.1388	77.1354	Equation VIII	
	A	7.2740×10^{6}	7.3152×10^{6}	R$_2$ mechanism	
	ΔS	–307.4169	–307.3700	Phase boundary reaction	1/2
	γ	0.9595	0.9595	Cylindrical symmetry	
II Stage	So rapid that could not be studied				
III Stage	E	14.7770	14.7770	Equation V	
	A	4.5333×10^{-2}	4.5333×10^{-2}	F$_1$ mechanism	
	ΔS	–467.7018	–467.7018	Random nucleation	1
	γ	0.9716	0.9716	Mampel equation	

E in kJ mol^{-1}, A in s^{-1}, ΔS in J mol^{-1} K^{-1}

Mn(II), Ni(II), Cu(II), and Zn(II) complexes decomposed in three stages whereas Co(II) complex decomposed in four stages. The first stage in all the above chelates represents the loss of 2–3 water molecules above 150°C. According to Nikolaev *et al.*[18], water eliminated above 150°C can be considered as coordinated water.

Initial decomposition temperature and inflection temperature have been used to determine the thermal stability of metal chelates. In the present course of studies, based on observations made by earlier workers[24], the relative thermal stabilities of the metal chelates can be given as

[Cu(LH)(OAc)$_2$(H$_2$O)$_3$] < [Co(LH)(OAc)$_2$(H$_2$O)$_3$] < [Ni(LH)(OAc)$_2$(H$_2$O)$_3$]
< [Zn(LH)(OAc)$_2$(H$_2$O)$_3$] < [Mn(LH)Cl(H$_2$O)$_4$]Cl.
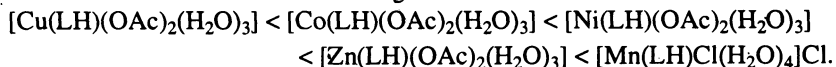
The total mass loss for each complex is in agreement with theoretical values and those obtained by independent pyrolytic experiment.

TABLE-8

KINETIC PARAMETERS FOR THE DECOMPOSITION OF $[Zn(LH)(OAc)_2(H_2O)_3]$ FROM
TG USING COATS-REDFERN EQUATION AND ACCEPTED MECHANISTIC EQUATIONS

Substance	Para-meters	From Coats-Redfern equation	From mechanitic equation	Reaction mechanism	Order of reaction
$[Zn(LH)(OAc)_2(H_2O)_3]$					
I Stage		So rapid that could not be studied			
II Stage	E	31.4122	31.4122	Equation V	
	A	1.6425	1.6425	F_1 mechanism	
	ΔS	−34.8920	−34.8920	Random nucleation	1
	γ	0.9742	0.9742	Mampel equation	
III Stage	E	20.9769	20.9769	Equation V	
	A	7.3346×10^{-2}	7.3346×10^{-2}	F_1 mechanism	
	ΔS	−58.9443	−58.9443	Random nucleation	
	γ	0.9754	0.9754	Mampel equation I	1

E in kJ mol^{-1}, A in s^{-1}, ΔS in J mol^{-1} K^{-1}

Decomposition Kinetics: From Tables 3–5, it can be seen that more than one equations give good linear curve with high value of correlation coefficient, so that it may become difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function $g(\alpha)$ which gives kinetic parameters in agreement with those obtained by the numerical method.

In the present case, it is observed that the values of E, A and ΔS for the second stage decomposition of $[Mn(LH)Cl(H_2O)_4]Cl$ and first stage decomposition of $[Ni(LH)(OAc)_2(H_2O)_3]$ obtained from Coats-Redfern with n = 1/3 are in good agreement with the corresponding values obtained for A_2 mechanism based on Random nucleation, Avrami equation 1.

First and fourth stage of the $[Co(LH)(OAc)_2(H_2O)_3]$ and the first stage of $[Cu(LH)(OAc)_2(H_2O)_3]$ follows 1/2 order of reaction. First stage decomposition of $[Co(LH)(OAc)_2(H_2O)_3]$ and $[Cu(LH)(OAc)_2(H_2O)_3]$ follows R_2 mechanism based on phase boundary reaction, cylindrical symmetry and the fourth stage decomposition of $[Co(LH)(OAc)_2(H_2O)_3]$ follows A_2 Mechanism based on Random nucleation, Avrami equation 1.

Order of the reaction is found to be 2/3 for the third stage of $[Mn(LH)Cl(H_2O)_4]Cl$ and for the second stage of $[Co(LH)(OAc)_2(H_2O)_3]$. Of these $[Mn(LH)Cl(H_2O)_4]Cl$ follows D_1 mechanism with one-dimensional diffusion and $[Co(LH)(OAc)_2(H_2O)_3]$ follows A_3 mechanism based on Random nucleation, Avrami equation II.

For the first stage decomposition of $[Mn(LH)Cl(H_2O)_4]Cl$ and third stage decomposition of $[Ni(LH)(OAc)_2(H_2O)_3]$ and $[Cu(LH)(OAc)_2(H_2O)_3]$ the values of kinetic parameters obtained for Coats-Redfern equation with n = 1 are in good agreement with those values obtained for F_1 mechanism based on random

nucleation (Mampel equation). Second and third stage decomposition of $[Zn(LH)(OAc)_2(H_2O)_3]$ also follows first order reaction which is in agreement with F_1 mechanism based on random nucleation.

All these mechanisms are proposed since the values of E, A and ΔS computed from the mechanistic equation agree well with those from the nonmechanistic equation (Coats-Redfern) having maximum correlation coefficient.

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