Thermal decomposition kinetics of Zn(II), Cd(II) and Pd(II) chelates of 5,5-dimethyl1,3-cyclohexanedionebis(thisemicarbazone)

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Abstract— **The Zn (II), Cd(II), and Pd (II) complexes were prepared from 5,5dimethyl1,3-cyclohexanedione bis (thiosemicarbazone) and subjected to heating at a rate of 20^0C per minute. The order of the reaction, mechanism, and kinetic parameters are studied using nine mechanistic and three nonmechanistic equations. The values of E, A, and ΔS were compared to choose the correct mechanism of decomposition.**

Index Terms— **[Zn(5,5DMe1, 3CHDTSC], [Cd(5, 5DMe1, 3CHDTSC)],[Pd(5,5Dme1,3CHDTSC)] 5,5-dimethyl1,3-cyclohexanedionebis(thiosemicarbazone), Dimedonebis (thiosemicarbazone).**

I. INTRODUCTION

The complexes of Zn (II), Cd(II), and Pd(II) of the ligand Dimedonebis(thiosemicarbazone) or 5,5-dimedone are prepared [1][2]by refluxing the resultant solution obtained by mixing the ligand and the metal ion. Sodium acetate is added to adjust the pH of the solution. The complexes formed are dried in a desiccator. The TG and DTG plots were recorded and analyzed for the determination of E, A, ΔS, and r(order). The mechanism of all stages is also arrived at. Zn complex decomposed in three stages while the Cd complex by two stages and Pd complex in a single stage. The order of decomposition of all stages was one. The nonmechanistic equation V is in agreement with the Coats Redfern equation rather than Horowitz –Metzger and Mac Callum Tanner equations. All steps followed random nucleation by the Mampel equation.

II. EXPERIMENT

PLOT OF TG and DTG of complexes.
The complexes were subjected to heating at a rate of $20\ ^0$ C in a platinum crucible in a static air atmosphere.TG and DTG plots were taken.
TREATMENT OF DATA.

Nine mechanistic equations proposed by Satava [3] were used to find out the order and kinetic parameters. The order of the reaction is arrived at by putting the values of n as 0.33, 0.5, 0.66, and 1 in the following equations.

$\ln [1-(1-\alpha)^{1-n} / (1-n)T^2]$ vs. $1/T$ for $n \neq 1$
and
$\log[-\log(1-\alpha)/T^2]$ vs. $1/T$ for $n = 1$.

The nine mechanistic equations proposed by Satava used for finding out kinetic parameters and the corresponding mechanisms of decomposition are given below.

Function	Equation	Rate-controlling process
D1	$\alpha^2 = kt$	One dimensional diffusion
D2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion, spherical symmetry, Jander equation[4]
D4	$(1-2/3\ \alpha)-(1-\alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry
F1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus on each particle, Mampel equation[5]
A2	$-\ln(1-\alpha)^{1/2} = kt$[5]	Random nucleation, Avrami equation 1[6]
A3	$-\ln(1-\alpha)^{1/3} = kt$[6]	Random nucleation, Avrami equation II.[6]
R2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry

The results of kinetic parameters obtained using the mechanistic equations are compared with the values arrived at by three nonmechanistic equations. The non-mechanistic equations considered are Coats

Redfern[7], [Horowitz-Metzger[8], andMac Callum Tanner[9].

Coats-Redfern equation[7]

$$\int_0^\alpha d\,\alpha/(1-\alpha)^n = A/\varphi \int_0^\alpha e^{(-E/Rt)}\,dT$$

Where α is mass loss at time t. Plot of $\log[1-(1-\alpha)^{1-n}/T$ vs. $1/T$ for $n \neq 1$ and $\log[-\log(1-\alpha)/T^2]\ 1/T$ for $n=1$ will be straight line for correct value of n. ΔS can be calculated using equation $A = kT_s/h\ e^{(\Delta s/R)}$ where T_s is peak temperature from DTG, h –Planck's constant, k- the Boltzmann constant.

Horowitz –Metzger equation[8]

The approximation method by Horowitz- Metzger equation was also used to arrive at the kinetic parameters.

$\ln[1-(1-\alpha)^{1-n}/1-n] = \ln ART_s^2/\varphi E - E/RT_s + \Theta E/RT_s^2$.

Where $\Theta = T-T_s$. The plot of the left-hand side with Θ will be linear from the slope of which E is calculated and A is the intercept.

Mac Callum Tanner Equation[9]

The nonmechanistic equation by Mac Callum was also used to find the kinetic parameters by plotting the left-hand side of the equation with $1/T$ for the nth order.

$\log[1-(1-\alpha)^{1-n}/(1-n)] = \log AE/\Theta R - 0.483E^{0.435}(0.449+0.217E/T)*10^3$

III RESULT AND DISCUSSION

The complexes of 5,5-dimethyl1,3 cyclohexanedionebis (thiosemicarbazone) with Zn(II) and Cd(II) has the formula [ZnL] and [CdL].The TG and DTG plots of the complexes are given below.

TG and DTG Traces of [ZnL]

TG and DTG Traces of [CdL]

TG and DTG Traces of [PdL]
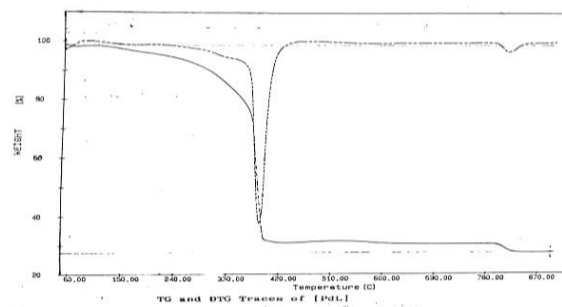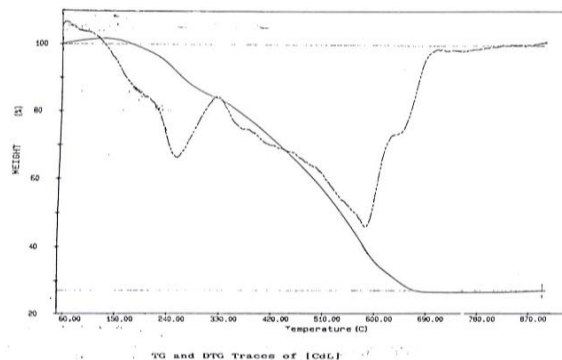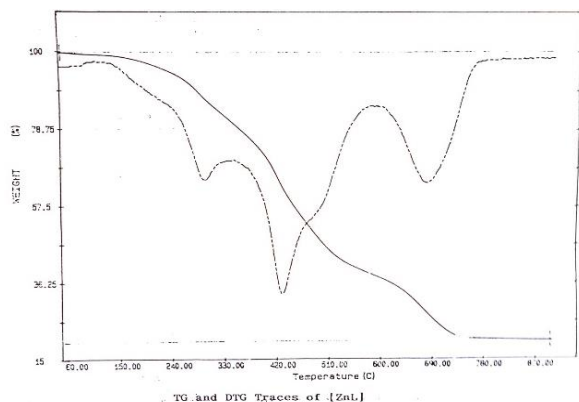
All the complexes [ZnL], [CdL], and [PdL] started the decomposition around 200^0C indicating the absence of any type of water molecule in the complexes.

[znL] decomposes in three steps. The first mass loss is $\approx$ at 330^0C due to the removal of the dimedone part. The second and third mass losses are due to the removal of the first and second thiosemicarbazone parts.

[CdL] followed two stages of decomposition pattern. Like [ZnL] the removal of the dimedone part happens first but at a lower temperature as evident from the plots. In the second stage, both the thiosemicarbazone parts are lost together unlike [ZnL]. The initial decomposition temperature of [ZnL] is higher compared to [CdL] proving that [ZnL] is more thermally stable compared to[CdL].In the case of [PdL], the decomposition happened in a single step. The final products formed after the complete decomposition are ZnO, CdO, and PdO. The thermal decomposition kinetics of three complexes follow the stability order as $[ZnL] \approx [pdL] < [CdL]$.

The kinetic parameters, ΔE, frequency factor A, and entropy of activation ΔS were calculated using the nine mechanistic equations put forward by Satava and are given in the tables. The order of decomposition of all the stages of all the complexes is one. Putting the value of n as one in Coats-Redfern, Horowitz – Metzger and Mac Callum equations, the kinetic parameters, ΔE, frequency factor A and entropy of

activation ΔS were calculated and are given in the tables. The values of the kinetic parameters arrived at by mechanistic and nonmechanistic equations are studied to arrive at the mechanism of decomposition. All the steps followed the F_1 mechanism based on the Mampel equation, the rate-controlling process being random nucleation, by the formation of a nucleus on each particle. The negative values of ΔS are indicative of the more ordered structure of activated complex than the reactants and the reactions are slower than normal.

IV. CONCLUSION

The decomposition steps of all stages are of the order of one. All the mechanisms of mass loss followed the F1 mechanism, by random nucleation and followed the equation V of the nonmechanistic equation. The kinetic parameters calculated using the nonmechanistic equation V are in agreement with the values arrived at by the Coats Redfern equation.

Complex	Parameter	Mechanistic equations								
		1	2	3	4	5	6	7	8	9
[ZnL]										
Stage 1	E	68.31	68.33	74.09	70.25	35.35	12.92	5.56	30.95	32.38
	A	6.05×10^2	1.15×10^3	1.09×10^3	4.16×10^2	3.43	1.64×10^{-2}	1.76×10^{-3}	5.27×10^{-1}	5.17×10^{-1}
	ΔS	-197.62	-192.27	-192.67	-200.74	-240.65	-285.10	-303.66	-256.23	-256.40
	R	0.9937	0.9954	0.9962	0.9957	0.9958	0.9926	0.9806	0.9945	0.9950
Stage 2	E	172.33	203.82	243.01	216.74	136.48	62.18	37.42	105.83	115.45
	A	1.1×10^{10}	1.45×10^{12}	3.40×10^{14}	3.23×10^{12}	5.86×10^7	1.30×10^2	1.33	1.26×10^{-2}	4.37×10^5
	ΔS	-59.58	-19.30	-237.09	-243.08	-103.50	-211.79	-249.93	-288.68	-144.25
	R	0.9521	0.9601	0.9882	0.9631	0.9718	0.9662	0.9588	0.9607	0.9648
Stage 3	E	76.993	87.03	100.79	92.20	49.56	17.23	6.46	39.68	42.83
	A	2.13×10	6.25×10	1.07×10^2	2.74×10	1.0651	6.48×10^{-3}	6.31×10^{-4}	9.85×10^{-2}	1.13×10^{-1}
	ΔS	-201.18	-199.04	-197.97	-200.68	-207.14	-217.28	-221.90	-211.87	-211.59
	R	0.9817	0.9798	0.9775	0.9790	0.9679	0.9380	0.8380	0.9704	0.9694
[CdL]										
Stage1	E	44.56	50.57	56.83	52.67	26.88	27.03	26.88	22.26	23.79
	A	1.59×10	3.95×10	4.64×10	1.53×10	6.59×10	3.41×10^{-1}	9.35×10^{-4}	8.65×10^{-2}	9.00×10^{-2}
	ΔS	-227.18	-219.61	-218.27	-227.46	-253.66	-259.14	-308.22	-270.55	-270.22
	R	0.9716	0.9769	0.9817	0.9787	0.9759	0.9795	0.9759	0.9696	0.9733
Stage2	E	75.59	80.80	87.26	82.49	44.21	44.21	44.21	39.27	40.86
	A	2.42×10^4	5.36×10^4	8.67×10^4	1.95×10^4	4.0×10	2.0×10	1.33×10	4.66	4.97
	ΔS	-169.81	-163.20	-159.20	-171.62	-223.11	-228.88	-232.23	-240.98	-240.45
	R	0.9441	0.9553	0.9557	0.9607	0.9706	0.9706	0.9706	0.9546	0.9608
[PdL]										
Stage1	E	107.30	114.48	122.22	113.36	57.91	23.87	12.52	52.23	54.08
	A	6.21×10^5	1.44×10^6	1.66×10^6	2.66×10^5	1.17×10^2	1.29×10^{-1}	9.42×10^{-3}	1.65×10	1.66×10
	ΔS	-142.11	-135.10	-133.90	-149.15	-213.47	-270.11	-176.96	-229.77	-229.70
	R	0.9965	0.9961	0.9956	0.9646	0.9627	0.9609	0.9573	0.9640	0.9636

E- KJmol^{-1} , A- S^{-1} , ΔS- J mol^{-1}K^{-1}. LH$_2$ - 5,5Dme1,3CHDTSC

	Temperature Ranges in TG (^{0}C) φ=10^{0}min^{-1}	Peak temperature in DTG (^{0}C)	% Loss of mass			Probable assignment of mass loss.
			TG	Theoretical	Pyrolysis	
[ZnL]						
Stage I	240-340	330	31.76	30.90	--	Dimedone
Stage II	370-460	440	25.84	25.00	--	1 thiosemicarbazone
StageIII	600-730	670	21.20	21.37	79.08	2 thiosemicarbazone
[CdL]						
Stage I	200-320	280	28.9	27.21	--	Dimedone +1 thiosemicarbazone.
Stage II	420-640	580	41.0	40.82	70.54	2 thiosemicarbazone
[PdL]						
Stage I	240-430	380	67.50	64.70	67.91	All ligand parts together.

Comp	Parameter	Coats Redfern equation	Horowitz Metzger equation	Mac Callum Tanner Equation	mechanistic equation	Followed mechanism
				[ZnL]		
Stage 1	E	35.45	51.43	44.90	35.35	Equation V
	A	3.43	1.6×10^2	7.89×10^3	3.43	F1 mechanism
	ΔS	-240.65	-208.65	-176.26	-240.65	Random nucleation
	R	0.9958	0.9962	0.9974	0.9958	Mampel equation
Stage 2	E	136.48	142.26	149.56	136.48	Equation V
	A	5.86×10^7	2.92×10^8	1.51×10^{11}	5.86×10^7	F1 mechanism
	ΔS	-103.50	-90.14	-38.16	-103.50	Random nucleation
	R	0.9718	0.9738	0.9761	0.9718	Mampel equation
Stage 3	E	49.56	70.04	64.89	49.56	Equation V
	A	1.065	2.38×10	5.34×10^3	1.065	F1 mechanism
	ΔS	-207.19	-228.26	-183.23	-207.19	Random nucleation
	R	0.9679	0.9834	0.9802	0.9679	Mampel equation
				[CdL]		
Stage 1	E	26.88	34.17	36.44	26.88	Equation V
	A	6.59×10^{-1}	7.53	1.89×10^3	6.59×10^{-1}	F1 mechanism
	ΔS	-253.66	-233.39	-187.41	-253.66	Random nucleation
	R	0.9759	0.9806	0.9893	0.9759	Mampel equation
Stage 2	E	44.21	88.90	49.39	44.21	Equation V
	A	4.0×10	1.55×10^3	6.46×10^4	4.0×10	F1 mechanism
	ΔS	-223.11	-192.61	-161.65	-223.11	Random nucleation
	R	0.9706	0.9591	0.9750	0.9706	Mampel equation
				[PdL]		
Stage 1	E	57.91	37.49	70.74	57.91	Equation V
	A	1.17×10^2	3.50	3.76×10^5	1.17×10^2	F1 mechanism
	ΔS	-213.47	-242.66	-146.28	-213.47	Random nucleation
	R	0.9627	0.9969	0.9958	0.9627	Mampel equation

E- KJmol^{-1}, A- S^{-1}, ΔS- J mol^{-1}K^{-1} . LH$_2$ – 5,5Dme1,3CHDTSC

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