THERMAL BEHAVIUOR OF Mn(II)
complex of dimedonebis(thiosemicarbazone)

Dr.Lali Thomas Kotturan[1]

[1], *Associate professor & HOD, Department of Chemistry, Little Flower College, Guruvayoor, Kerala.*
Corresponding Author: Dr.Lali Thomas Kotturan [1]

ABSTRACT: The paper deals with the thermal decomposition process of Mn(II) complex of the ligand 5,5- dimethyl1,3-cyclohexanedionebis(thiosemicarbazone) [dimedonebis(thiosemicarbazone)]. The TG and DTG curves obtained by heating the complex in a static air atmosphere at a heating rate of 20^0 per minute non -isothermally are studied. The order of the decomposition of all stages of the complex is found to be one. The decomposition kinetics of each step are found using nine mechanistic equations by Satava and three non-mechanistic equations such as Coats Redfern, Horowitz – Metzger, and Mac Callum Tanner equations. The mechanism of all decomposition was by Mampel equation, F1 mechanism of random nucleation.

KEYWORDS:
5,5dimethylcyclohexnedionebis(thiosemicarbazone), dimedone bis (thiosemicarbazone), mechanistic and nonmechanistic equations, kinetic parameters.

I. INTRODUCTION

Thermogravimetry is the art of weighing a substance during its heating up. In this paper, Mn(II) ion is chelated with the ligand 5,5dimethylcyclohexanedionebis(thiosemicarbazone) and subjected to the process of heating and weighing. The data obtained was studied for its stability, mechanism of decomposition, kinetic parameters activation energy(E), frequency factor (A), entropy change (ΔS), and order r.

[1][2] The ligand was prepared by refluxing the alcoholic solutions of dimedone and thiosemicarbazide dissolved in hydrochloric acid for one hour and cooling. The complex was synthesised by adding slowly the hot aqueous solution of the metal salt to the refluxing alcoholic solution of dimedone and continuing the reluxion. The manganese complex was separated within five minutes.

[3] Mechanism of the thermal decomposition of the non-isothermal method has been reported by Satava. The non-isothermal process occurs at a faster rate in a very small period allowing Arrhenius type equation

$$d\alpha/dt = A\, e^{(-E)/RT}\, f(\alpha) \ldots\ldots\ldots(1)$$

where A-pre exponential factor, t-time, $f(\alpha)$ - the factor depends on the mechanism of the process. A series of nine $f(\alpha)$ forms have been proposed which is given in Table 1.

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	$[1-(1-\alpha)^{1/3}]^2 = kt$ [7]	Three dimensional diffusion, spherical symmetry, Jander equation[7]
D4	$(1-2/3\,\alpha)-(1-\alpha)^{2/3} = kt$ [7]	Three dimensional diffusion, spherical symmetry
F1	$-\ln(1-\alpha) = kt$ [8]	Random nucleation, one nucleus on each particle, Mampel equation[8]
A2	$-\ln(1-\alpha)^{1/2} = kt$[10]	Random nucleation, Avrami equation 1[9]
A3	$-\ln(1-\alpha)^{1/3} = kt$[10]	Random nucleation, Avrami equation II.[9]

R2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry

Integrating the equation (1) can be written in the general form

$$\ln g(\alpha)/T^2 = \ln AR/\varphi E - E/RT \dots\dots(2)$$

Linear plots were drawn for nine forms E, A, and ΔS were calculated. The order of the reaction is found by comparing the correlation coefficient (r) of plots inserting the values 0.33,0.5,0.66 and 1 for n 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 $n = 1$.

[4] The Coats –Redfern equation is an integral method for finding A, E, and ΔS by putting the correct value of n.

$$\int_0^\alpha d\alpha/(1-\alpha)^n = A/\varphi \int_0^\alpha e^{(-E/Rt)} dT \dots\dots(3)$$

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-Boltzmann constant.

[5The approximation method using Horowitz- Metzger equation also was followed to arrive at the kinetic parameters.
$\ln[1-(1-\alpha)^{1-n}/1-n] = \ln ART_s^2/\varphi E - E/RT_s + \Theta E/RT_s^2$
………(4). 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.

[6]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.
$\log[1-(1-\alpha)^{1-n}/(1-n)] = \log AE/\Theta R - 0.483E^{0.435}(0.449+0.217E/T)*10^3$ ………(5).

II. EXPERIMENTATION
The ligands and the complex $[MnL(H_2O)_2]$ (where LH_2 is 5,5-dimethyl1,3-cyclohexane dione bis(thiosemicarbazone) or dimedonebis (thiosemicarbazone) are prepared and subjected to heating at a rate of 20^0 min^{-1} in a static air atmosphere. The products are confirmed to be oxides by x-ray studies.

The data is subjected to mechanical and nonmechanistic equations explained earlier and found out the order and kinetic parameters.

III.OBSERVATIONS AND DISCUSSION
The TG and DTG plots of the complexes are given below.

TG and DTG Traces of $[MnL(H_2O)_2]$
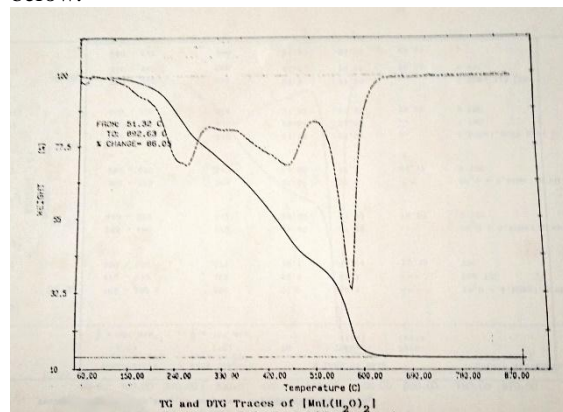
The complex is represented as $[MnL(H_2O)_2]$. The plot shows no detectable change upto 100^0C showing the absence of water of hydration. The decomposition occurred in three stages the final product being Mn_3O_4, which was characterized by X-ray pattern. The complex is thermally stable as indicated by the initial thermal decomposition temperature. The decomposition starts at 160^0C and form oxide at 580^0C. The first stage of decomposition is the removal of the coordinated water molecule, followed by the dimedone part and thiosemicarbazide part. In the case Mn(II) complex the two dimedone parts get detached one following the other giving two corresponding peaks. The decomposition weight loss and the probable assignment of loss are explained in the table. The kinetic parameters were calculated by the three non mechanistic equations and with nine mechanistic equations. Comparing the values of parameters, the mechanism is confirmed. Equation V of the mechanistic equation is selected which follows the F1 mechanism, Random nucleation, Mampel equation. The Calculated parameters of each step are given in Table. All decomposition reactions were of the order of one.

[MnL(H$_2$O)$_2$]	Temperature Ranges in TG (^{0}C) φ=10^{0}min^{-1}	Peak temperature in DTG (^{0}C)	% Loss of mass			Probable assignment
			TG	Theoretical	Pyrolysis	
Stage 1	162-330	262	37	38.3	--	2 H$_2$O + dimedone
Stage 2	370-510	462	22.8	23.7	--	One TSC
Stage 3	530-580	571	19.7	18.04	70.10	Second TSC

Complex [MnL(H$_2$O)$_2$]	Parameter	Coats Redfern equation	Horowitz Metzger equation	Mac Callum Tanner Equation	mechanistic equation	Followed mechanism
Stage 1	E A ΔS R	35.28 6.44 -234.42 0.9931	46.95 251 -203.95 0.9847	44.39 13700 -170.64 0.9963	35.28 6.44 -234.42 0.9931	Equation V F1 mechanism Random nucleation Mampel equation
Stage 2	E A ΔS R	79.78 937 -194.42 0.9707	67.61 2430 -186.49 0.9706	91.62 2130000 -130.10 0.9753	79.78 937 -194.42 0.9707	Equation V F1 mechanism Random nucleation Mampel equation
Stage 3	E A ΔS R	128.25 1220000 -137.09 0.9652	149.46 14700000 -116.37 0.9747	142.88 4050000000 -69.66 0.9712	128.25 1220000 -137.09 0.9652	Equation V F1 mechanism Random nucleation Mampel equation

E- KJmol^{-1} , A- S^{-1} , ΔS- J mol^{-1}K^{-1}

Complex	Parameter	Mechanistic equations								
		1	2	3	4	5	6	7	8	9
[MnL(H$_2$O)$_2$]										
Stage 1	E A ΔS r	66.26 3380 -182.32 0.9872	70.11 5080 -178.93 0.9901	77.42 7660 -175.52 0.9818	71.54 1690 -188.04 0.9911	35.28 6.44 -234.42 0.9931	13.47 0.0260 -280.28 0.9868	6.20 0.0270 -299.12 0.9868	32.02 1.21 -248.32 0.9883	30.55 0.53 -255.09 0.9410
Stage 2	E A ΔS r	142.36 1.08*10^7 -116.59 0.9628	151.22 2.75*10^7 -108.84 0.9676	161.51 4.03*10^7 -105.66 0.9712	154.84 1.18*10^7 -115.82 0.9685	79.78 9.37*10^2 -194.42 0.9707	33.76 0.365 -259.71 0.9590	18.42 0.0194 -284.13 0.9395	72.15 110 -212.24 0.9637	74.62 11700 -211.73 0.9662
Stage 3	E A ΔS r	125.24 297000 -148.87 0.9915	160.90 1.25*10^3 -194.33 0.9858	212.36 3.83*10^{10} -50.97 0.9767	177.64 1.55*10^8 -96.79 0.9826	128.25 1.22*10^6 -137.09 0.9652	57.28 15.8 -230.72 0.9573	33.62 0.285 -264.14 0.9462	86.73 4.6*10^{-4} -317.54 0.9779	99.26 3.77*10^3 -185.19 0.9737

E- KJmol^{-1} , A- S^{-1} , ΔS- J mol^{-1}K^{-1}

IV. CONCLUSION

The ligand dimedonebis (thiosemicarbazone) forms stable complexes with the metal ion Mn(II). The decomposition happens in three steps and all are of the order of one following the random nucleation process. The end product is Mn$_3$O$_4$. The complex is thermally stable up to 160^{0}C.

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