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Kinetics and Mechanism of the Thermal Decomposition of Schiff Base Complexes of Cobalt and Nickel by TG AND DSC Studies

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The thermal decomposition of cobalt(II) and nickel(II) chelates of dibenzoylmethane thiosemicarbazone (DBMTSC) was studied by TG and DSC studies. The mechanism of the decomposition has been established from TG data. The kinetic parameters, *viz.*, activation energy E, preexponential factor A, and order of reaction n, were calculated from the TG curves using mechanistic and non-mechanistic 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 cobalt and nickel complexes of a novel Schiff base, dibenzoylmethane thiosemicarbazone. Non-isothermal 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 $[ML(H_2O)_3]$ where L = dibenzoylmethane thiosemicarbazone (DBMTSC) and M = Co(II) or Ni(II).

EXPERIMENTAL

The ligand was prepared from dibenzoylmethane and thiosemicarbazide following the reported procedure by Schiff. Samples of cobalt(II) and nickel(II) chelates of dibenzoylmethane thiosemicarbazone were prepared by adding ethanolic solution of the ligand to the metal chloride solution in 1 : 1 ratio. The mixture was refluxed and 1.5 gm of sodium acetate added. Boiled further and the precipitates were filtered, washed with ethanolic solution of the reagent and dried in vacuum desiccator.

The purity of the samples was checked by elemental analysis for the metal and C, H, N analysis. The structure of these two chelates was found to be $[M(DBMTSC)(H_2O)_3]$ where M = Co(II) or Ni(II).

The IR spectra were recorded using a Perkin-Elmer model 283 infrared spectrophotometer. Thermal analyses 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. The infrared spectra of the chelates indicate the absence of characteristic absorption for the –OH group and a shift in ν(C=N,) showing that –OH group and C=N are involved in coordination. The absence of bands in the region 2650–2500 cm^{-1} in the free ligand indicates that it exists in the thioketo form in the solid state. However, during the complex formation it might exist in the enol form. This is indicated by the absence of the band due to C=S of the ligand in the complexes and the appearance of a new band on complexation around 660 cm^{-1} which can be attributed to ν(C–S). Characteristic bands of H_2O are present in the spectra of two complexes. 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 curve for $[CoL(H_2O)_3]$ exhibited a three stage decomposition pattern and that for $[NiL(H_2O)_3]$ exhibited a two stage decomposition pattern. The first stage of decomposition was rapid change for $[NiL(H_2O)_3]$ and could not be subjected to kinetic analysis. The second stage represents the major decomposition step in the second case and 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[18] and Satava[19]. 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 the preexpontential factor, t is the time and f(α) depends on the mechanism of the process. For a linear heating rate ϕ, dT/dt = ϕ 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

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

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 of equation (3), the temperature integral, which is an incomplete gamma function, was used in the form given by Coats and Redfern[20] which is one of the best solutions recommended by several authors.[21, 22]

The general form of the equation used is

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

Along with the mechanistic equations two non-mechanistic methods suggested by Coats and Redfern[20] and Horowitz and Metzger[23] were also used for comparison. The reaction order can easily be estimated by comparing the values using n = 0.33, 0.5, 0.66 and 1 in equations.

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

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

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

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

RESULTS AND DISCUSSION

The decomposition temperature ranges for 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 Table 3. The corresponding values of E, A and r from non-mechanistic equations (Coats-Redfern, Horowitz-Metzger) are given in Table 4.

The DTG and DSC curves for $[CoL(H_2O)_3]$ give a single well defined peak in the third stage of decomposition. The overall loss of mass from the curve is 80.84% while the theoretical loss in mass for the conversion of $[CoL(H_2O)_3]$ to Co_3O_4 is 80.68%.

TABLE 1
THERMAL DECOMPOSITION DATA

Substance	Peak temp. in DTG °C	Peak temp. in DSC °C	Temp. ranges in DTG °C	Loss of mass %			Probable assignments
				From TG	Theoretical	Pyrolysis	
$[CoL(H_2O)_3]$							
I Stage	110	110 (s)	50–120	8.33	8.8		Loss of $2H_2O$
II Stage	310	310 (s)	120–350	26.2	26.24		Loss of $1H_2O$ + TSC
III Stage	410	410 (s)	350–450	45.8	45.64	80.9	Loss of DBM part
	470	470 (w)	450–480				
$[NiL(H_2O)_3]$							
I Stage	250	250 (s)	225–300	35.8	35		Loss of $3H_2O$ + TSC
II Stage	475	475 (s)	300–500	45.8	47.09	81.8	Loss of DBM part.

TABLE 2
KINETIC EQUATIONS

Function	Equation	Rate-controlling process
D_1	$\alpha^2 = Kt$	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha = Kt$	Two-dimesional diffusion, cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = Kt$	Three-dimensional diffusion, spherical symmetry: Jander equation
D_4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3} = Kt$	Three-dimensional diffusion, spherical symmetry: Ginstling-Brounshtein equation
F_1	$-\ln(1-\alpha) = Kt$	Random nucleation, one nucleus on each particle: Mampel equation
A_2	$-\ln(1-\alpha)^{1/2} = Kt$	Random nucleation: Avrami equation I
A_3	$-\ln(1-\alpha)^{1/3} = Kt$	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

In the case of $[NiL(H_2O)_3]$ a two stage decomposition pattern is observed. The main decomposition stage is represented by DTG and DSC peaks at 475°C and 470°C respectively. Mass loss at the end of this stage, read from the TG curve, is 81.6%. X-ray diffraction study shows that the final stage is NiO. The theoretical mass loss at this stage for the decomposition of $[NiL(H_2O)_3]$ to NiO would be 82.09%. If we assume that the other decomposition products have completely volatilized off, water eliminated above 150°C can be considered as coordinated water.

Decomposition Kinetics

From Tables 3 and 4 it can be seen that more than one equation give good linear curve with high value of correlation coefficient, so that it may become

TABLE 3
KINETIC PARAMETERS FOR THE DECOMPOSITION OF [Co(DBMTSC)(H_2O)3] AND (Ni(DBMTSC)(H_2O)3 FROM TG USING MECHANISTIC EQUATIONS

Substance	Para-mates	1	2	3	4	5	6	7	8	9
	E	104.6796	119.5246	139.0113	125.9232	66.6683	33.0982	18.9587	60.0537	64.8516
[Co(DBMTSC)(H_2O)]	A	6.6525×10^6	1.1480×10^8	2.5247×10^9	1.1572×10^8	1.0293×10^4	2.1776×10^5	2.3904×10^6	3.0799×10^3	2.059×10^3
	ΔS	–119.9706	-96.2707	-70.5527	-96.2038	–164.3353	–148.4232	–128.4877	–182.1124	–187.2054
II Stage	r	0.9953	0.9983	0.9988	0.9989	0.9957	0.9946	0.9930	0.9989	0.9987
	E	81.0197	97.7602	120.4595	105.1716	66.7412	27.3725	142.4936	48.6638	54.2304
	A	3.169×10^3	1.0929×10^4	1.8802×10^5	1.0114×10^4	1.0118×10^4	2.9511×10^6	1.3713×10^8	3.9578×10^5	2.3953×10^5
III Stage	ΔS	–184.9385	–174.6365	–150.9625	–175.2818	–175.2787	–128.0514	-96.1090	–144.7690	–148.9477
	r	0.9344	0.9526	0.9697	0.9697	0.9761	0.9644	0.9424	0.9532	0.9626
	E	42.3289	49.8395	58.3128	52.1843	28.6378	8.4263	2.2706	22.0211	24.2959
[Ni(DBMTSC)(H_2O)]	A	1.0678×10^6	4.9460×10^5	4.4235×10^5	1.4440×10^6	2.3557×10^6	2.0468×10^7	1.5838×10^7	1.475×10^7	1.5095×10^7
II Stage	ΔS	–137.266	–143.6709	–144.5999	–134.7551	–130.6830	–112.6927	–144.8262	–115.4178	–115.2263
	r	0.9793	0.9709	0.9692	0.9739	0.9474	0.8830	0.8921	0.9618	0.9574

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

TABLE 4
KINETIC PARAMETERS FOR THE DECOMPOSITION OF $CoL(H_2O)_3]$AND $[NiL(H_2O)_3]$ FROM TG USING NONMECHANISTIC EQUATIONS.

Substance	Coats-Redfern				Horowitz-Metzer				
	E	A	ΔS	r	E	A	ΔS	R	order n.
$[CoL(H_2O)_3]$									
II-Stage	60.0265	1.923×10^4	–168.6186	0.9956	74.7006	2.1496×10^4	–167.6910	0.9984	1/2
III-Stage	66.6683	1.0293×10^4	–175.1359	0.9751	70.2285	3.85×10^2	–202.4787	0.9771	1
$[NiL(H_2O)_3]$									
II Stage	19.3481	1.1377×10^7	–117.5793	0.9467	38.3575	2.349×10^1	–226.505	0.9826	1/3

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

difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function g(α) which gives kinetic parameters in agreement with those obtained by the numerical method. In the present case, it is observed that for the second stage of Co(II) complex, and second stage of Ni(II) complex, E and A values obtained from the LR equation are in good agreement with the E and A values obtained for the R_2 mechanism on a phase boundary reaction Cylindrical symmetry $F_{1.}$ mechanism gives the maximum correlation for the third stage of decomposition of $[CoL(H_2O)_3]$

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