Asian Journal of Chemistry Vol. 18, No. 4 (2006), 2562–2566

Thermal Decomposition Kinetics and Mechanism of Ni(II),Co(II) and Mn(II) Complexes of N,N′-Diethyleneamine-bis(3-caboxypropenamide)

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The thermal decomposition behaviour of Ni(II), Co(II) and Mn(II) complexes with nitrogen and oxygen donor ligand N,N′-diethyleneamine-bis(3-caboxypropenamide) [$DBCPH_2$] has been studied using TG and DTG analysis. The phenomenological and kinetic aspects of the TG curves are investigated for the evaluation of kinetic parameters such as activation energy, pre-exponential factor and entropy of activation using Coats-Redfern equation. The mechanism for the decomposition stages is found to be either random nucleation or one-dimensional diffusion. There is no regular variation in the values of kinetic parameters for the decomposition of these complexes. Kinetic parameters using Coats-Redfern equation and the mechanism based kinetic equations are found to be in good agreement with each other in almost all cases.

Key Words: Kinetics, Thermal, Ni(II), Co(II) and Mn(II) complexes, N,N′-diethylene-amine-bis(3-caboxypropenamide).

INTRODUCTION

Studies on thermal decomposition and kinetics of metal complexes have been carried out by several workers[1, 2]. Wendlandt[3] and Hill[4] studied the thermal properties of metal chelates with different types of complexing ligands. Synthesis and characterization of complexes of polydentate ligands containing amide groups have been reported[5]. In continuation of our work[5], the present communication reports the thermal decomposition behaviour of the Ni(II), Co(II) and Mn(II) complexes of a polydentate ligand N,N′-diethyleneamine-bis(3-caboxypropenamide) derived from maleic anhydride and diethylene triamine.

EXPERIMENTAL

All the chemicals used were of AR grade or pure quality. The solvents were double distilled before use. The ligand N,N′-diethyleneamine-bis(3-caboxypropenamide) ($DBCPH_2$) was prepared by literature method[5]. Thermogravimetric analyses were carried out on Shimadzu TGA-50H thermal analyzer system in an atmosphere of nitrogen (sample mass 5 mg and heating rate 10 K min^{-1}).

RESULTS AND DISCUSSION

The complexes were characterized by metal and anion estimation, molecular mass determination, elemental analysis, magnetic susceptibility, conductance measurements in acetonitrile, methanol and nitrobenzene and infrared electronic spectral studies. The complexes had the general formula [M(DBCP)] where M = Ni(II), Co(II) or Mn(II). Based on the above studies a coordination number of six is suggested for the metal ions. The ligand acts as a pentadentate and the sixth coordination is satisfied through a weak interactions between the metal ion and the carbonyl group of the neighbouring ligand. These complexes show three stages of decomposition (Figs. 1–3).

The [Ni(DBCP)] complex is thermally stable up to 240°C and undergoes three stage decomposition (Table-1) in the range 240–320, 330–400 and 430–520°C as indicated by the DTG peaks at 272, 427.3 and 500.4°C respectively.

The [Co(DBCP)] complex is stable up to 230°C and also undergoes three stages of decomposition in the range 230–320, 360–460 and 470–560°C as indicated by DTG peaks at 264.6, 397 and 510.8°C respectively.

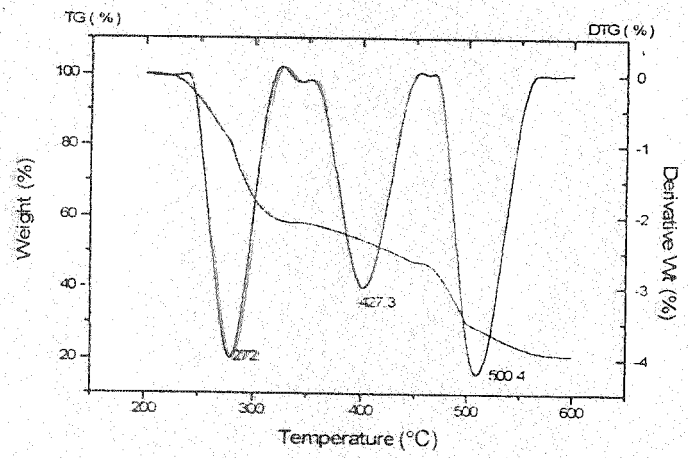

Fig. 1. TG and DTG curves of [Ni(DBCP)]

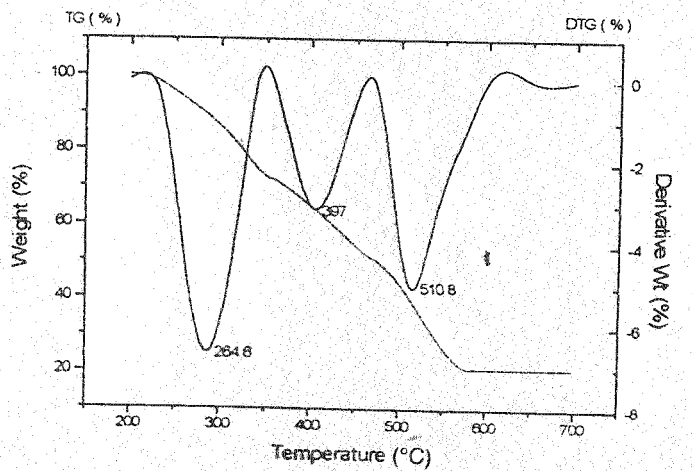

Fig. 2. TG and DTG curves of [Co(DBCP)]

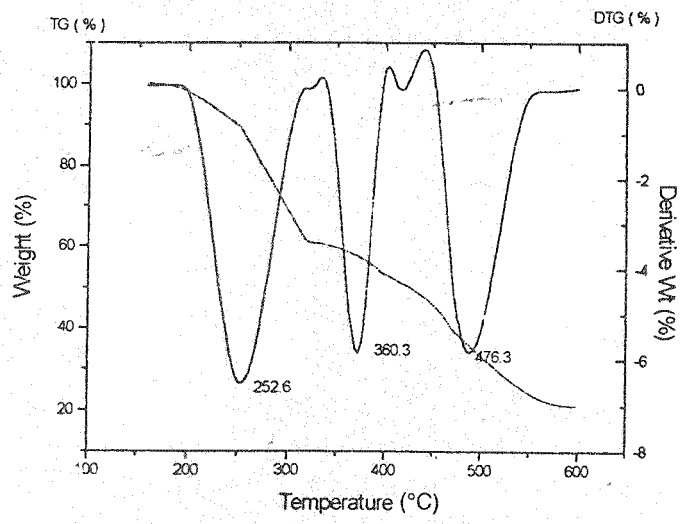

TABLE-1
THE THERMAL DECOMPOSITION DATA OF THE COMPLEXES OF Ni(II), Co(II) AND Mn(II) WITH [$DBCPH_2$]

Complexes	TG plateaux (°C)	DTG peaks (°C)	DTG peak widths (°C)	Final residue at 700°C	Final mass		
					Final TG (%)	Independent pyrolysis	Theoretical
[Ni(DBCP)]	Upto 240 Above 520	272.0 427.3 500.0	240–320 330–400 420–520	NiO	20.2	20.8	20.98
[Co(DBCP)]	Upto 230 Above 560	264.6 397.0 510.8	230–320 360–460 470–560	Co_2O_3	21.8	21.2	21
[Mn(DBCP)]	Upto 225 Above 550	252.6 360.3 476.3	225–305 330–420 460–550	Mn_2O_3	22	22	21.8

The [Mn(DBCP)] complex is stable up to 225°C and undergoes decomposition in three stages in the ranges 225–305, 340–420 and 460–550°C and is indicated by the DTG peaks at 252.6, 360.3 and 476.3°C, respectively.

These complexes are stable up to 225°C. The final plateau occurs above 560°C after which there is no mass loss in the TG curve. The final residue in each case is found to be the corresponding metal oxide, which is in conformity with the mass loss data obtained from TG curve, independent pyrolysis and theoretical value.

The final product in each case indicates that during different decomposition steps the ligand is removed from the complex. The complexes show the same thermal decomposition pattern suggesting the same structure for all these complexes. The complexes are stable in the order Mn < Co < Ni which may be attributed to decrease in size.

Kinetic aspect

The kinetic parameters of the thermal decomposition of complexes were evaluated using a computer programme. In all these complexes, the different stages altogether include the decomposition of the ligand part. The Coats-Redfem[6] equation was used for calculating the kinetic parameters such as the activation energy (E), the pre-exponential factor (A) and entropy of activation. The equation is

$$\log g(\alpha)/T^2 = \log [AR/\phi E (1 - 2RT/E)] - E/2.303\ RT$$

In the present work $\log g(\alpha)/T^2$ *vs.* 1/T gave a straight line in each case of the thermal decomposition stages and slope and intercepts are used to calculate kinetic parameters by the least square method. Eventually the correlation coefficient tested the goodness of fit. The entropy of activation Δs can be calculated using the equation

$$A = \frac{kT_s e^{\Delta S/R}}{h}$$

where k is the Boltzmann's constant and h the Planck's constant.

The kinetic parameters for the thermal decomposition reactions of the complexes are given in Table-2. The values are useful in assigning the strength of the bond in the complexes. The activation energy ranges from 214–340 kJ/mol. These values are greater than the activation energy for the dehydration of hydrated salts[7, 8]. This indicates that the ligands are strongly coordinated to the metal ions. The Δs values are negative for all the complexes indicating that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal[9, 10].

TABLE-2
KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITIONS

Complex	Stages	E (kJ mol^{-1})	A (S^{-1})	Δs (J K^{-1} mol^{-1})	r	n
[Ni(DBCP)]	I	261.6	1.6×10^{16}	–61.88	0.9984	1.33
	II	240.08	2.84×10^{11}	–84.97	0.9949	1.40
	III	331.96	2.86×10^{16}	–63.82	0.9981	1.70
[Co(DBCP)]	I	214.8	4.11×10^{11}	–25.80	0.9975	1.20
	II	231.75	2.56×10^{9}	–71.40	0.9982	1.60
	III	330.9	9.8×10^{15}	–135.60	0.9985	1.40
[Mn(DBCP)]	I	298.99	2.96×10^{9}	–166.12	0.9983	1.50
	II	239.6	4.32×10^{10}	–127.50	0.9979	1.90
	III	288.9	1.02×10^{11}	–76.00	0.9987	1.10

The mechanism based kinetic equations have been used to determine the mechanism of decomposition and to calculate the parameters for the various decomposition stages of the three complexes. In the present investigation, nine forms of $g(\alpha)$ codified by Satava have been used. The form of $g(\alpha)$ repressing the best experimental data is considered as the mechanism of the reaction. The

mechanisms for the three stages of Ni(II) and Co(II) and the first stage of Mn(II) complexes is the Mampel model representing random nucleation. In these cases the highest value of correlation coefficient was for $g(\alpha) = -\ln(1-\alpha)$. In the case of the second and third stages of decomposition of Mn(II) complex the mechanisms were one-dimensional diffusion because in these cases out of the nine values best correlations were obtained when $g(\alpha) = \alpha^2$. The values obtained for the various kinetic parameters using Coats-Redfem equations and the mechanism based kinetic equations are found to be in good agreement with each other in almost all cases. The correlation coefficients calculated for all the decomposition stages show near perfect fit with linearity. Generally the values of r are found to be closer to unity with Coats-Redfern equation than the mechanism based kinetic equations.

ACKNOWLEDGEMENTS

The author is thankful to Dr. G. Krishnan, Reader and Head, Department of Chemistry, University College, Thiruvananthapuram, for his valuable guidance and suggestions and to UGC for the award of teacher fellowship.

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(*Received*: 28 May2005; *Accepted:* 10 April 2006) AJC-4764