Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 583–590

KINETIC AND THERMODYNAMIC PARAMETERS OF THE THERMAL DECOMPOSITION OF ZINC(II) DIALKYLDITHIOCARBAMATE COMPLEXES

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Abstract

The thermodynamic and kinetic parameters of the thermal decomposition of $Zn(S_2CNR_2)_2$ complexes (R=CH_3, C_2H_5 and n-C_3H_7) were determined with the dynamic thermogravimetric method. Superimposed TG/DTG/DSC curves show that thermal decomposition reactions for chelates with R=C_2H_5 and n-C_3H_7 occur in the liquid phase, at temperatures far away from their melting points, whereas for the complex with R=CH_3 the thermal decomposition begins at a temperature closer to its melting point, suggesting a rather complex decomposition mechanism.

Keywords: dithiocarbamates, thermal decomposition, zinc

Introduction

The thermal decomposition mechanism of solid dialkyldithiocarbamates [$M(CS_2CNR_2)_n$; M=metal] shows a particular behavior: differently from most solid metal complexes that decompose in the solid phase, metal dialkyldithiocarbamates decompose in the liquid phase at temperatures far away from their melting points [1–3].

In the present work the kinetic and thermodynamic parameters for the thermal decomposition of $Zn[S_2CN(CH_3)_2]_2$, $Zn[S_2CN(C_2H_5)_2]_2$ and $Zn[S_2CN(n\text{-}C_3H_7)_2]_2$ were determined using a non-isothermal method.

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Zn(II) dialkyldithiocarbamate complexes were synthesized from direct reaction of $ZnCl_2$ with appropriated dialkylammonium compounds in acetone, as described in more detail elsewhere [4–7].

After purification, the complexes were vacuum dried and characterized by different techniques, such as melting point determination, thermal analysis (TG, DTG and DSC), infrared spectroscopy, mass spectroscopy and elemental analysis.

The melting points were obtained with a Microquimica equipment model MQAPF 301 and a differential scanning calorimeter Shimadzu-model DSC-50. The infrared spectra, in the 4000–400 cm^{-1} region, were obtained with a Bomem spectrometer, model MB-102; samples were mixed with KBr and pressed to form pellets. Mass spectra were obtained with a Varian (model MAT 311) spectrometer, at ionization energy of 70 eV. The elemental analysis for C, H and N were performed with a Perkin Elmer CHN analyzer, model PE 2400.

The dynamic thermogravimetric curves were obtained in a Shimadzu Thermobalance model TGA-50, under nitrogen atmosphere, at 50 mL min^{-1} carrier gas flow and initial sample masses 5.0±0.7 mg, in the range of 25–500°C, with heating rates of 5, 10 and 15°C min^{-1}.

Results and discussion

Characterization of complexes

The melting temperature values obtained either by the conventional method or by DSC determination were rather similar (Table 1).

Table 1 Melting points obtained by conventional and DSC measurements

Complexes	Melting temperatures/°C	
	Conventional method	DSC
$Zn[S_2CN(CH_3)_2]_2$	252.7–253.0	253.4
$Zn[S_2CN(C_2H_5)_2]_2$	178.8–180.6	180.6
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	113.5–115.5	114.5

As summarized in Table 2, infrared spectra show typical bands of a complex formation, particularly due to the presence of strong stretching ν(C–N) vibration bands in the range 1480–1550 cm^{-1}, similarly to those observed for a number of dithiocarbamate complexes [8, 9]. In addition, the lower wavenumber for the ν(C–S) stretching band and an isolated band near 1000 cm^{-1} indicate that the ligand is bidentately bound to the metal.

Table 2 Principal absorption bands observed in the infrared spectra

Complexes	Attribution			
	C=N	N–C=S	=C–S	C–S
$Zn[S_2CN(CH_3)_2]_2$	1522.6(s)	1242.8(s)	1050.4(w)	973.2(s)
$Zn[S_2CN(C_2H_5)_2]_2$	1503.0(s)	1272.2(s)	1073.0(s)	994.0(s)
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	1498.0(s)	1241.1(s)	1088.6(m)	974.6(m)

s=strong; m=medium; w=weak

Table 3 Elemental analysis for the complexes

Complexes	mass% (calculated)			mass% (experimental)		
	C	H	N	C	H	N
$Zn[S_2CN(CH_3)_2]_2$	23.6	3.9	9.2	23.7	3.6	9.3
$Zn[S_2CN(C_2H_5)_2]_2$	33.2	5.6	7.7	33.4	5.7	7.8
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	40.2	6.7	6.7	40.4	6.3	6.8

The elemental compositions (Table 3) are in agreement with expected data from stoichiometric formulae of the complexes.

The mass spectra data for all complexes were obtained with sample insertion by direct probe injection. The intensities of molecular ions $[ML_2]^+$ and the loss of ligand molecules suggest the following order of stability:

$$Zn[S_2CN(C_2H_5)_2]_2 > Zn[S_2CN(n\text{-}C_3H_7)_2]_2 > Zn[S_2CN(CH_3)_2]_2$$

Thermal behavior

The superimposed TG/DTG curves presented similar shapes with a single step correspondent to decomposition of ligand. The mass loss was calculated stoichiometrically (Table 4). The superimposed TG/DTG/DSC curves of $Zn[S_2CN(C_2H_5)_2]_2$ and $Zn[S_2CN(n\text{-}C_3H_7)_2]_2$ complexes suggested thermal decomposition beginning in the liquid phase and for $Zn[S_2CN(CH_3)_2]_2$ complex suggested thermal decomposition beginning in the solid phase, at a temperature close to the melting point, followed by an expressive amount of decomposition occurring in the liquid phase.

According to the beginning temperature of the decomposition of complexes the following order of thermal stability may be proposed:

$$Zn[S_2CN(C_2H_5)_2]_2 < Zn[S_2CN(CH_3)_2]_2 < Zn[S_2CN(n\text{-}C_3H_7)_2]_2$$

Figure 1 shows the dynamic thermogravimetric curve for the complex $Zn[S_2CN(C_2H_5)_2]_2$. Figures 2 and 3 show TG/DTG/DSC typical superimposed curves for $Zn[S_2CN(C_2H_5)_2]_2$ and $Zn[S_2CN(CH_3)_2]_2$ complexes, respectively.

As it can be seen from Figs 2 and 3 (DSC curves) there is an endothermic peak near 90°C, probably due to a loss of residual water molecules; in Fig. 3 the DSC

Table 4 Thermal stability of the zinc(II) complexes

Complexes	Temperature range/° C	Mass loss/ %	
		Calculated	Experimental
$Zn[S_2CN(CH_3)_2]_2$	236.2–353.5	92.9	94.1
$Zn[S_2CN(C_2H_5)_2]_2$	231.9–368.0	97.0	97.0
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	238.8–367.4	96.1	96.2

curve shows two peaks which are attributed to the thermal decomposition of $Zn[S_2CN(CH_3)_2]_2$, as discussed above.

Dynamic thermal decomposition kinetic

The kinetic parameters for the $Zn[S_2CN(R)_2]_2$ complexes were calculated from the non-isothermal TG curves, with heating rates of 5, 10 and 15°C min^{-1}, according to the well known expression proposed by Coats–Redfern [10]:

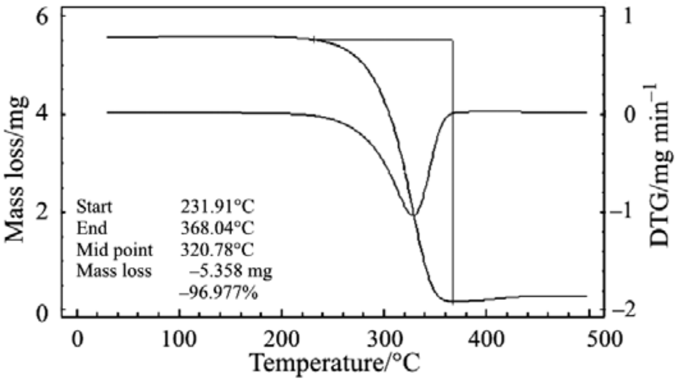

Fig. 1 Dynamic TG curve for $Zn[S_2CN(C_2H_5)_2]_2$

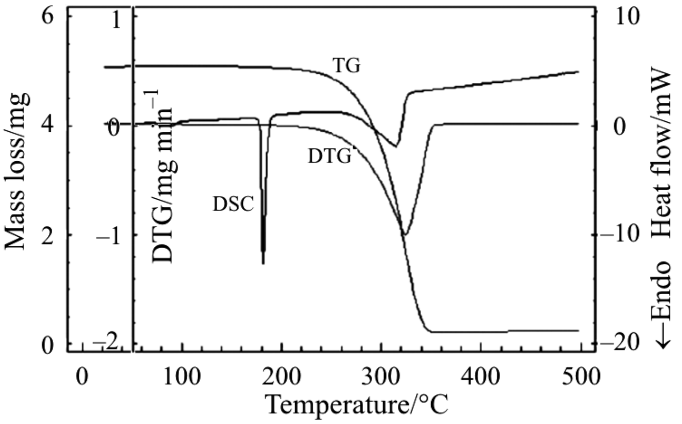

Fig. 2 Superimposed TG/DTG/DSC curves for $Zn[S_2CN(C_2H_5)_2]_2$

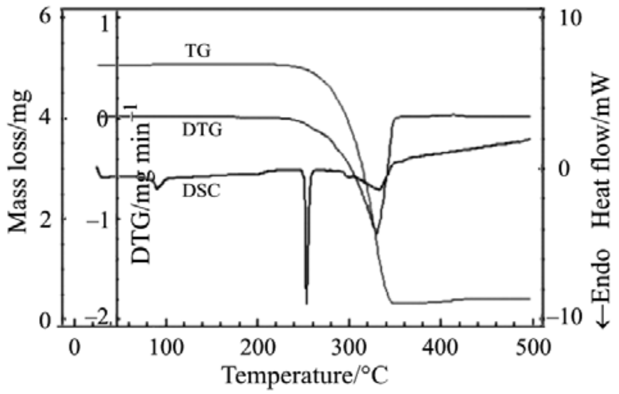

Fig. 3 Superimposed TG/DTG/DSC curves for $Zn[S_2CN(CH_3)_2]_2$

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{\Phi E}-\frac{E}{RT} \tag{1}$$

where T accounts for absolute temperature, E – apparent activation energy, A – pre-exponential factor, R – gas constant, Φ – heating rate and $g(\alpha)$ – kinetic model.

The kinetic model that best fitted the experimental curves was the one-dimensional phase-boundary controlled model (R_1), within the range of decomposed fraction $0.95\geq\alpha\geq0.15$.

Table 5 Kinetic parameters according to the Coats–Redfern equation

Complexes	Kinetic parameters	Heating rates		
		5°C min^{-1}	10°C min^{-1}	15°C min^{-1}
$Zn[S_2CN(CH_3)_2]_2$	n	0.39	0.38	0.47
	E/kJ mol^{-1}	121.97	110.20	110.06
	A/s^{-1}	2.85E+07	1.87E+06	1.82E+06
	r	0.9997	0.9997	0.9999
$Zn[S_2CN(C_2H_5)_2]_2$	n	0.23	0.28	0.58
	E/kJ mol^{-1}	113.80	106.18	120.89
	A/s^{-1}	4.46E+06	6.91E+06	1.61E+07
	r	0.9999	1.0	0.9999
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	n	0.44	0.49	0.47
	E/kJ mol^{-1}	123.76	116.89	118.03
	A/s^{-1}	2.57E+07	6.35E+06	5.82E+06
	r	0.9993	0.9998	0.9998

The kinetic parameters (n – reaction order; E – apparent activation energy, A – pre-exponential factor) were calculated according to the expressions proposed by Coats–Redfern (CR) [10], Madhusudanan (MD) [11], Horowitz–Metzger (HM) [12] and Van Krevelen (VK) [13]. The CR and MD integral methods gave similar results with correlation coefficients equal or better than 0.999, while the HM and VK approach methods showed kinetic parameter values somewhat higher than those for CR and MD methods, due to different mathematical treatment (Tables 5–8).

Table 6 Kinetic parameters according to the Madhusudanan equation

Complexes	Kinetic parameters	Heating rates		
		5°C min^{-1}	10°C min^{-1}	15°C min^{-1}
$Zn[S_2CN(CH_3)_2]_2$	n	0.47	0.30	0.50
	E/kJ mol^{-1}	126.48	106.76	111.76
	A/s^{-1}	8.45E+07	9.43E+05	2.84E+06
	r	0.9996	0.9999	0.9999
$Zn[S_2CN(C_2H_5)_2]_2$	n	0.26	0.31	0.59
	E/kJ mol^{-1}	115.37	107.76	121.70
	A/s^{-1}	6.85E+06	1.05E+06	2.05E+07
	r	0.9998	0.9999	0.9999
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	n	0.34	0.43	0.44
	E/kJ mol^{-1}	118.98	114.07	116.77
	A/s^{-1}	9.51E+06	3.68E+06	4.80E+06
	r	0.9995	0.9996	0.9997

Table 7 Kinetic parameters according to the Horowitz–Metzger equation

Complexes	Kinetic parameters	Heating rates		
		5°C min^{-1}	10°C min^{-1}	15°C min^{-1}
$Zn[S_2CN(CH_3)_2]_2$	n	0.58	0.41	0.41
	E/kJ mol^{-1}	147.86	128.14	131.12
	A/s^{-1}	8.42E+09	8.52E+07	1.14E+08
	r	0.9994	0.9998	0.9998
$Zn[S_2CN(C_2H_5)_2]_2$	n	0.27	0.36	0.69
	E/kJ mol^{-1}	133.32	126.53	142.12
	A/s^{-1}	2.01E+08	5.33E+07	1.40E+09
	r	0.9995	0.9999	0.9998
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	n	0.53	0.56	0.60
	E/kJ mol^{-1}	145.17	135.49	140.48
	A/s^{-1}	2.42E+09	3.59E+08	6.43E+08
	r	0.9996	0.9998	0.9997

Thermodynamic parameters

The thermodynamic activation parameters for the zinc(II) chelates (Table 9) were estimated according to the Coats–Redfern equation, applied in the determination of kinetic model, and the following expressions:

$$\Delta H^{\#} = E - RT_{\text{s}} \tag{2}$$

Table 8 Kinetic parameters according to the Van Krevelen equation

Complexes	Kinetic parameters	Heating rates		
		5°C min^{-1}	10°C min^{-1}	15°C min^{-1}
$Zn[S_2CN(CH_3)_2]_2$	n	0.48	0.32	0.32
	E/kJ mol^{-1}	140.09	114.05	115.37
	A/s^{-1}	5.05E+14	1.45E+12	1.93E+12
	r	1.0	0.9943	0.9943
$Zn[S_2CN(C_2H_5)_2]_2$	n	0.25	0.42	0.62
	E/kJ mol^{-1}	114.98	124.32	130.24
	A/s^{-1}	1.90E+12	1.20E+13	4.14E+13
	r	0.9667	1.0	0.9991
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	n	0.48	0.49	0.54
	E/kJ mol^{-1}	133.79	123.77	130.30
	A/s^{-1}	7.64E+13	9.58E+12	2.77E+13
	r	0.9989	0.9989	0.9999

$$\Delta S^{\#} = R\left(\ln\frac{Ah}{kT_{\mathrm{s}}} - 1\right) \tag{3}$$

$$\Delta G^{\#} = \Delta H^{\#} - T_{\mathrm{s}}\Delta S^{\#} \tag{4}$$

where $\Delta H^{\#}$ – activation enthalpy, $\Delta S^{\#}$ – activation entropy, $\Delta G^{\#}$ – Gibbs activation free energy, h – Planck constant, k – Boltzmann constant and T_{s} – observed peak temperature.

Table 9 Thermodynamic activation parameters for the $Zn(S_2CNR_2)_2$ complexes

Complexes	$\Delta S^{\#}$/J mol^{-1} K	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta G^{\#}$/kJ mol^{-1}
$Zn[S_2CN(CH_3)_2]_2$	–106.48	110.60	175.36
$Zn[S_2CN(C_2H_5)_2]_2$	–126.01	89.49	165.97
$Zn[S_2CN(n\text{-}C_3H_7)_2]_2$	–106.24	112.35	176.70

The estimated thermodynamic activation parameters are indicative of an endothermic process related to an irreversible thermal decomposition suggesting a better molecular orientation in the activated state. Similar results were obtained by Kurup *et al.* and Straszko *et al.* in studies on thermal decomposition of different solid-state systems [14, 15].

Conclusions

The thermal decomposition of the complexes $Zn[S_2CN(CH_3)_2]_2$, $Zn[S_2CN(C_2H_5)_2]_2$ and $Zn[S_2CN(n\text{-}C_3H_7)_2]_2$ occurs in a single step, following the same phase boundary reaction of the unidimensional R_1 model, at temperatures far from their characteristic melting points, except for the methyl compound that decomposes only partially in the solid phase. The estimated thermodynamic activation parameters indicate the occurrence of an irreversible thermal decomposition through an endothermic process, and a better molecular orientation in the activated state.

* * *

The authors acknowledge CAPES and CNPq Foundations (Brazil) for scholarships and financial support.

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