SThermal Decomposition Kinetics of Dialkyldithiocarbamates by Using the Isothermal Thermogravimetry

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Abstract: The thermal decomposition kinetics of solid Zinc(II) bis(dialkyldithiocarbamate) complexes, $Zn(S_2CNR_2)_2$, where R= $i-C_3H_7$, $n-C_4H_9$, $i-C_4H_9$ and $n-C_5H_{11}$, were studied by using isothermal thermogravimetric heating technique. Results show that the thermal decomposition of these complexes occurs in a homogeneous liquid phase, after melting, according to a unidimensional phase-boundary reactions model, R_1. The thermal stability was found to be in the following order: $Zn(S_2CNBu^i_2)_2 < Zn(S_2CNPr^i_2)_2 < Zn(S_2CNBu^n_2)_2 < Zn(S_2CNPe^n_2)_2$.

Key words: Zinc, dithiocarbamates, isothermal decomposition, heating technique, thermal stability

INTRODUCTION

The main interest on the dithiocarbamates chemistry lies on their analytical and industrial potentiality. Even though the thermochemistry of metal dithiocarbamates is well documented, very little is still known about their thermal decomposition kinetics (Souza *et al.*, 2002).

We have recently studied a series of metal (Cd(II), Pd(II) and In(III)) bis(dialkyldithiocarbamates) (Souza *et al.*, 2002; Machado *et al.*, 1999; Range *et al.*, 1999) and found that for most of these complexes, the thermal decomposition occurs in the liquid phase, in a range of temperatures far away from their respective melting points, suggesting that the overall reactions should not be complicated by partial liquefaction occurring in a confined and restricted zone, as it is usually observed.

In the present research, the kinetics of thermal decomposition of Zinc (II) bis(dialkyldithiocarbamates), $Zn(S_2CNR_2)_2$, where R = $i-C_3H_7$, $n-C_4H_9$, $i-C_4H_9$ and $n-C_5H_{11}$ were studied using isothermal heating technique.

MATERIALS AND METHODS

Materials: The metal complexes were synthesized as described in the literature (Cavell *et al.*, 1979; Dias *et al.*, 1994; Carvalho *et al.*, 1992; Souza *et al.*, 1991, 1994) i.e., by direct reaction of $ZnCl_2$ with the appropriated dialkyldithiocarbamate dialkylammonium salt and were characterized by different techniques, such as melting point determination, infrared molecular absorption, mass spectrometry and elemental chemical analysis.

Melting points were determined with a Microquimica (model MQAPF 301) equipment. Infrared spectra were recorded between 4000 and 400 cm^{-1} with a Bomem (model MB 102) spectrometer; samples were mixed with KBr and pressed to form pellets.

Spectroscopic analysis: Mass spectra were obtained with a Varian (model MAT 311) spectrometer and ionization energy of 70 keV. The elemental analysis for C, H and N were performed with Perkin-Elmer C-H-N analyser, model PE 2400.

Thermal analysis: Isothermal thermogravimetric curves were obtained with a Shimadzu thermobalance model TA 50, under nitrogen atmosphere, at 50 $mLmin^{-1}$ carrier gas flow and initial sample masses around 5.0 ± 0.7 mg.

Differential scanning calorimetric measurements were performed in a Shimadzu DSC 50 calorimeter, under nitrogen atmosphere (50 mL min^{-1}), in the range of 25-500°C, with a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The melting temperatures obtained either by the conventional method or by DSC measurements lead to similar values, as shown in Table 1.

As summarized in Table 2, infrared spectra show the expected band as a consequence of complex formation: v(C-N) for the dialkyldithiocarbamate in the region 1480-1550 cm^{-1}, v(C-S) near 1000 cm^{-1}, suggesting that the ligand is bidentately coordinated to the metal (Bonati and Ugo, 1967).

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

The mass spectra results suggest the presence of the parent ion with intensities of 100%, 83.4%, 100% and 51.7% for the di-iso-propyl, di-n-butyl, di-iso-butyl and di-n-pentyl metal complexes and the following order of stability:

$$Zn(S_2CNPr^i_2)_2 = Zn(S_2CNBu^i_2)_2 >$$
$$Zn(S_2CNBu^n_2)_2 > Zn(S_2CNPe^n_2)_2$$
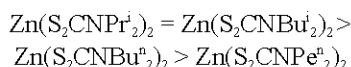
Thermal behavior: The superimposed TG/DTG/DSC curves present similar shapes with a well defined single step, indicating that the thermal decomposition occurs in the liquid phase, in temperature ranges far away from the melting points of the complexes (Fig. 1), according to the following thermal stability order:

$$Zn(S_2CNBu^i_2)_2 < Zn(S_2CNPr^i_2)_2 <$$
$$Zn(S_2CNBu^n_2)_2 < Zn(S_2CNPe^n_2)_2$$

Thermal decomposition kinetics: A series of five isothermal experiments was run in temperature ranges far away from the melting points of the Zinc (II) complexes. The chosen temperatures were 242, 247, 252, 257 and 262 °C for $Zn(S_2CNPr^i_2)_2$; 254, 259, 264, 269 and 274°C for $Zn(S_2CNBu^n_2)_2$; 241, 246, 251, 256 and 261 °C for $Zn(S_2CNBu^i_2)_2$ and 274, 279, 284, 289 and 294 °C for $Zn(S_2CNPe^n_2)_2$. These temperature ranges were deduced from TG dynamic curves.

The isothermal decomposition data were treated by the linear model:

$$g(\alpha) = kt + k_0 \qquad (1)$$

Where k_0 is related to the induction period.

The R1 model, related to the unidimensional limitrophe phase-reaction mechanism, for $0.95 \geq \alpha \geq 0.15$ interval, was found to best fit to the experimental data for all four complexes, with linear regression coefficients of about r = 0.999 or better and rendered lowest standard deviations (Table 4).

The kinetic parameters were calculated according to the Arrhenius equation:

$$k = Ae^{-E/RT} \qquad (2)$$

Where k is the rate constant reaction, A is the pre-exponential factor and E the apparent activation energy. Results are shown in Table 5.

The Fig. 2 and 3 show typical fraction decomposition reaction (α) versus time (t) plot and isothermal TGA curve, respectively.

Table 1: Melting points obtained by conventional and DSC measurements

Compounds	Melting Temperatures/°C	
	Conventional method	DSC
$Zn(S_2CNPr^i_2)_2$	234.0-235.7	234.7
$Zn(S_2CNBu^n_2)_2$	107.7-109.9	109.1
$Zn(S_2CNBu^i_2)_2$	112.0-114.0	113.7
$Zn(S_2CNPe^n_2)_2$	78.9-79.7	79.6

Table 2: Main infrared absorption bands

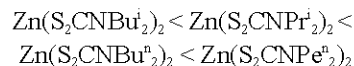| Compounds	Attributions			
	$C=N$	$N-C=S$	$=C-S$	$C-S$
$Zn(S_2CNPr^i_2)_2$	1482.5(s)	1193.3(m)	1038.1(m)	944.5(w)
$Zn(S_2CNBu^n_2)_2$	1495.7(s)	1186.9(w)	1094.0(m)	958.0(m)
$Zn(S_2CNBu^i_2)_2$	1497.2(s)	1199.4(w)	1089.7(w)	986.6(w)
$Zn(S_2CNPe^n_2)_2$	1505.7(s)	1151.3(w)	1096.9(w)	961.4(w)

s = strong, m = medium and w = weak

Table 3: Elemental analysis for the complexes

Compounds	Wt % (calculated)			Wt % (experimental)		
	C	H	N	C	H	N
$Zn(S_2CNPr^i_2)_2$	40.2	6.7	6.7	40.2	6.7	6.8
$Zn(S_2CNBu^n_2)_2$	45.6	7.6	6.0	45.8	7.1	6.1
$Zn(S_2CNBu^i_2)_2$	45.6	7.6	6.0	45.6	7.1	6.5
$Zn(S_2CNPe^n_2)_2$	49.8	8.3	5.3	49.8	8.4	5.5

Table 4: Kinetic model and calculated rate constants for the complexes

$Zn(S_2CNPr^i_2)_2$		242°C	247°C	252°C	257°C	262°C
R1	k (s⁻¹)	6.78E-05	0.9995	1.07E-04	0.9967	1.60E-04
	r	0.9995	2.03E-04	0.9996	2.51E-04	0.9996
$Zn(S_2CNBu^n_2)_2$		254°C	259°C	264°C	269°C	274°C
R1	k (s⁻¹)	6.31E-05	0.9999	7.71E-05	0.9999	1.06E-04
	r	0.9999	1.27E-04	0.9999	1.64E-04	0.9999
$Zn(S_2CNBu^i_2)_2$		241°C	246°C	251°C	256°C	261°C
R1	k (s⁻¹)	8.17E-05	0.9997	1.05E-04	0.9996	1.37E-04
	r	0.9995	1.62E-04	0.9997	2.19E-04	0.9998
$Zn(S_2CNPe^n_2)_2$		279°C	284°C	289°C	294°C	299°C
R1	k (s⁻¹)	1.11E-04	0.9999	1.21E-04	0.9999	1.46E-04
	r	0.9999	2.02E-04	0.9999	2.09E-04	0.9999

Table 5: Kinetic parameters calculated according the Arrhenius plot, for R_1 model

Complexes	Parameters		
	E $(kJmol^{-1})$	A (s^{-1})	r
$Zn(S_2CNPr^i_2)_2$	189.52	1.73E+08	0.9764
$Zn(S_2CNBu_2^n)_2$	114.76	1.56E+08	0.9948
$Zn(S_2CNBu_2^i)_2$	105.49	1.55E+08	0.9962
$Zn(S_2CNPe_2^n)_2$	110.18	1.57E+08	0.9975
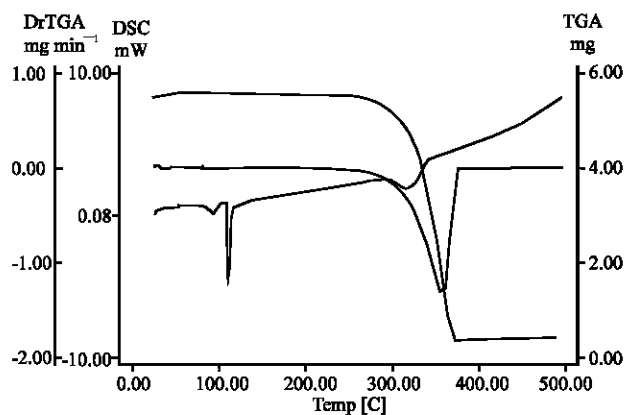
Fig. 1: Superimposed TG/DTG/DSC curves of Zn $(S_2CNBu^n_2)_2$ complex
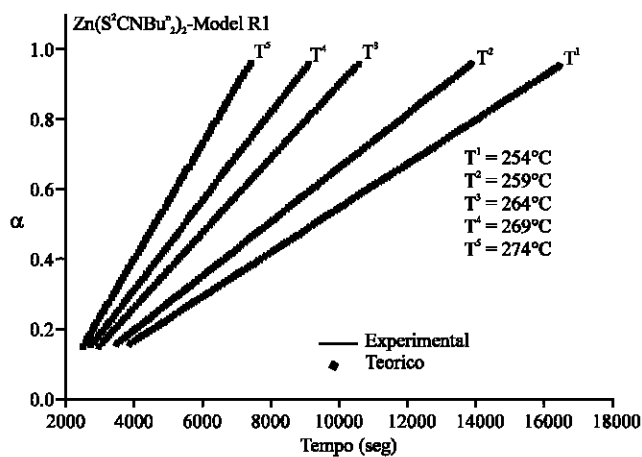
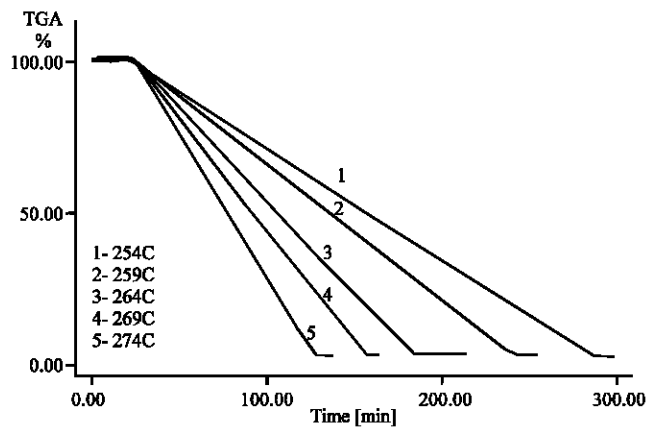Fig. 2: Typical α versus t curve for $Zn(S_2CNBu^n_2)_2$ Complex, according the R_1 model

Fig. 3: TG curve of $Zn(S_2CNBu^n_2)_2$

CONCLUSION

The superimposed TG/DTG/DSC curves show that the thermal decomposition of $Zn(S_2CNR_2)_2$ complexes occurs in the liquid phase, far away from their melting points, following the same phase-boundary reaction of the unidimensional R_1 model. This behavior is similar to that observed for the series $Cd(S_2CNR_2)_2$, $Pd(S_2CNR_2)_2$ and $In(S_2CNR_2)_3$ previously elsewhere studied.

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