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Kinetic study of the thermal decomposition on bis(dialkyldithiocarbamate) Cd(II) complexes by isothermal and non-isothermal thermogravimetry

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Abstract

The thermal decomposition kinetics of solid $Cd(S_2CNR_2)_2$ complexes, where $R{=}C_2H_5$, n-C_3H_7, n-C_4H_9 and iso-C_4H_9, has been studied using isothermal and non-isothermal thermogravimetry. Superimposed TG/DTG/DSC curves show that thermal decomposition reactions occur in the liquid phase. The kinetic model that best adjusted the experimental isothermal TG data was the one-dimensional phase-boundary reaction controlling process R_1. The thermal analysis data suggest the thermal stability sequence $Cd(S_2CNBu^n_2)_2 > Cd(S_2CNPr^n_2)_2 > Cd(S_2CNBu^i_2)_2 > Cd(S_2CNEt_2)_2$, according to the order of stability of apparent activation energy. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry; Cadmium; Thermal decomposition; Dialkyldithiocarbamate; Kinetics

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1. Introduction

The interest in the chemistry of dithiocarbamates lies in the analytical purpose of these compounds, as well as in their industrial applicability [1–5]. The thermochemistry of metal dithiocarbamates has been widely studied in the last years [6–10] but little is known about their thermal decomposition kinetics. In addition, these solid metal complexes were found to decompose in the liquid phase in a range of temperature far away from their respective melting points, and as a consequence, it is expected that the overall reactions should not be complicated by the partial liquefaction occurring in a confined and restricted zone, as usually observed.

In the present work we propose to study the kinetics of the thermal decomposition of bis(dialkyldithiocarbamates) of cadmium(II), $Cd(S_2CNR_2)_2$, where R= C_2H_5 (Et), n-C_3H_7 (Pr^n), n-C_4H_9 (Bu^n) and iso-C_4H_9 (Bu^i) using isothermal and non-isothermal heating methods.

2. Experimental

All operations involved in the preparations and purifications were carried out either in vacuo or in a dry-box in an atmosphere of dried nitrogen for air-sensitive compounds.

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2.1. Chemicals

The solvents used in all preparations were distilled and stored over Linde 4A molecular sieves. Diethylamine, di-*n*-propylamine, di-*n*-butylamine and di-isobutylamine (Merck) and carbon disulphide (Merck) were distilled, respectively. The cadmium(II) chloride was purified and dried in vacuo.

2.2. Preparations

The compounds $Cd(S_2CNR_2)_2$, where (R=ethyl, *n*-propyl, *n*-butyl and iso-butyl) were prepared by slowly adding a solution of dialkylammonium dialkyldithiocarbamate $\lfloor H_2NR_2 \rfloor \lfloor S_2CNR_2 \rfloor$ salt in acetone to a stirred solution of the $CdCl_2$ in acetone in 1:2 molar proportions. After filtration, the crystals formed were washed with petroleum ether (303–333 K), which were recrystallized from acetone and dried in vacuo, with yields in the range 83–87%. The complexes obtained were stored in a desiccator over calcium chloride.

2.3. Physical measurements

The melting temperatures for all compounds were determined by means of a Microquímica model MQAPF-301 apparatus. Microanalysis for carbon, hydrogen and nitrogen were obtained by Perkin-Elmer, elemental analyser, model PE-2400. The analysis of cadmium was made in GBC atomic absorption spectrophotometer, model 908-AA. Infrared spectra were recorded as KBr pellets, in the region 4000–200 cm^{-1} using a Bomem, model MB-102 series FT-IR spectrophotometer, mass spectra of the ligand and chelates on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV, at 523 K.

2.4. Thermal measurements

Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance, under nitrogen atmosphere, by isothermal and non-isothermal heating techniques. The carrier gas flow was always 3.33 $cm^3 s^{-1}$, the sample masses were 5.0±0.5 mg, the temperature in which the thermogravimetric isothermal curves were made are between the interval of 533–578 K for the complex $Cd(S_2CNEt_2)_2$, 533–583 K for $Cd(S_2CNPr^n_2)_2$, 538–588 K for $Cd(S_2CNBu^n_2)_2$, and 528–578 K for $Cd(S_2CNBu^i_2)_2$ and the heating rates were 5 and 10 K min^{-1} for non-isothermal experiments.

The differential scanning calorimetric curves were obtained in nitrogen atmosphere, using a differential scanning calorimeter Shimadzu model DSC-50, with a heating rate of 10 K min^{-1}.

The kinetic parameters in the dynamic heating method were determined according the Coats–Redfern [11] equation, using the thermal decomposition model suggested by the data obtained in the isothermal heating experiments.

3. Results and discussion

The microanalysis for nitrogen, carbon, hydrogen and cadmium (atomic absorption) of the complexes, $[Cd(S_2CNR_2)_2]$, with R=C_2H_5, *n*-C_3H_7, *n*-C_4H_9, and *i*-C_4H_9, are in good agreement with the expected values for compounds as shown in Table 1. The melting temperatures observed are well defined, as indicated in Table 1. The mode of coordination of the dialkyldithocarbamate and the definite melting points suggest the existence of very stable compounds. The νCN band assumes a double-band character which is

Table 1
Results of melting points (T_M), mass percentage analysis of C, H, N (%) and atomic absorption of Cd (%) and C–N and C–S stretching wave numbers (cm^{-1})

Complexes	T_M (K)	Calculated				Experimental				C=N	C=S
		C	H	N	Cd	C	H	N	Cd		
$Cd(S_2CNEt_2)_2$	523	29.37	4.93	6.85	27.48	29.02	4.87	6.84	25.89	1496.59	1073.31
$Cd(S_2CNPr^n_2)_2$	424	36.15	6.06	6.02	24.17	36.20	6.10	5.85	23.98	1495.73	1100.13
$Cd(S_2CNBu^n_2)_2$	410	41.48	6.95	5.37	21.56	41.51	6.82	5.61	20.85	1495.78	1093.17
$Cd(S_2CNBu^i_2)_2$	437	41.48	6.95	5.37	21.56	41.76	6.74	5.42	20.93	1486.66	1090.84

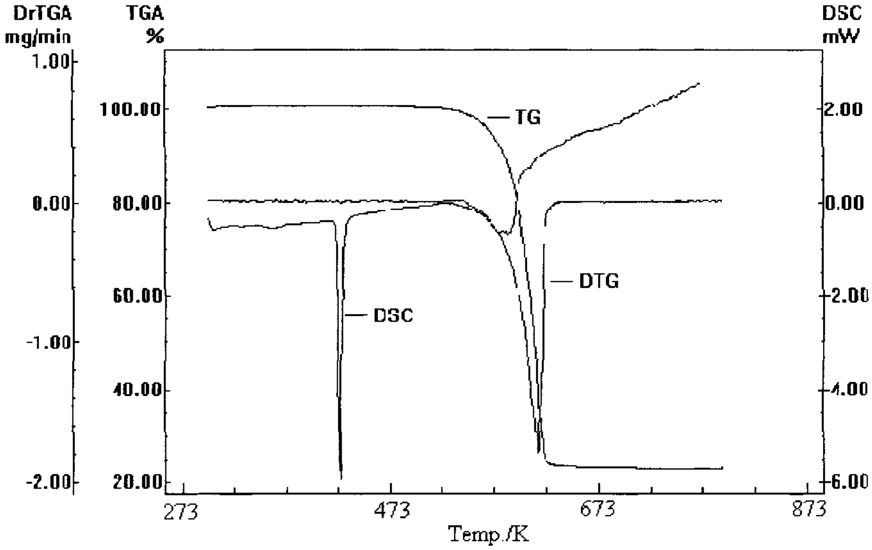

Fig. 1. Superimposed TG/DTG/DSC curves of complex $Cd(S_2CNPr^n_2)_2$.

reflected in the appearance of a stretching band shifted to a higher frequency. For all complexes this band frequency is higher than that of the respective ligand. On the other hand, a decrease in the νCS stretching band is observed and an isolated band near 1000 cm^{-1} indicates that the ligand is bonded in a bidentate manner to the metal [7–10,12]. The principal infrared bands observed are listed in Table 1. The mass spectra of the complexes revealed the presence of the parent ions with the following order of stability: $Cd(S_2CNEt_2)_2 > Cd(S_2CNPr^n_2)_2 > Cd(S_2CNBu^n_2)_2 > Cd(S_2CNBu^i_2)_2$. The intensities of the peaks observed are 13.43%, 10.82%, 6.65% and 5.00%, respectively.

Fig. 1 shows the typical TG/DTG and DSC curves for the thermal behaviour of $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$ compound. As shown by the DSC curve, the thermal decomposition begins at temperatures significantly higher ($\sim$363 K) than the melting point of the compound, and so in the liquid phase, in a single-stage process as suggested by the TG/DTG curves. The same behaviour was found for all the three other complexes, as shown in Table 2. The thermal decomposition data obtained in the dynamic TG experimental, listed in Table 2, together with those obtained in DSC measurements are in good agreement with the following scheme for the thermal decomposition reactions for the bis(dialkyldithiocarbamate) Cd(II) complexes

$$\begin{aligned} Cd(S_2CNR_2)_2(cr) &\rightarrow Cd(S_2CNR_2)_2(l) \\ &\rightarrow S_2CNR_2(g) + SCNR_2(g) + SCd(cr) \end{aligned}$$

Table 2
Thermal decomposition results

Complexes	Experimental conditions	Stage	Reaction internal (K)	Mass-loss (%)
$Cd(S_2CNEt_2)_2$	(1)[a]	1	498–613	78.6
	Residue		>693	21.4
	(2)[b]	1	506–628	76.8
	Residue		>693	23.2
$Cd(S_2CNPr^n_2)_2$	(1)[a]	1	505–618	76.0
	Residue		>693	24.0
	(2)[b]	1	520–634	76.3
	Residue		>693	23.7
$Cd(S_2CNBu^n_2)_2$	(1)[a]	1	516–626	75.1
	Residue		>693	24.9
	(2)[b]	1	526–636	77.0
	Residue		>693	23.0
$Cd(S_2CNBu^i_2)_2$	(1)[a]	1	503–616	85.4
	Residue		>693	14.6
	(2)[b]	1	509–633	83.7
	Residue		>693	16.3

[a] (1) Sample mass around 5 mg, heating rate 5 K min^{-1}, nitrogen (33.3 cm^3 s^{-1}).

[b] (2) Sample mass around 5 mg, heating rate 10 K min^{-1}, nitrogen (33.3 cm^3 s^{-1}).

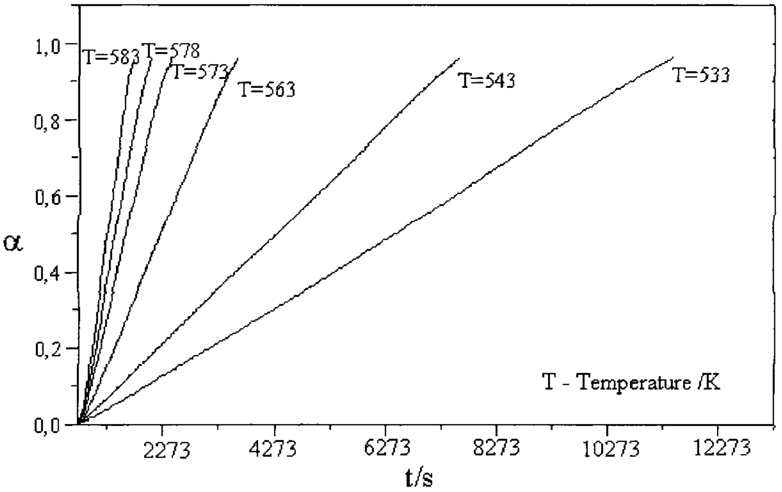

Fig. 2. Isothermal decomposition of $Cd(S_2CNPr^n_2)_2$.

The cadmium complexes decompose after melting in a single-stage process by partial loss of the ligands leaving the cadmium sulphide as residue. The isothermal mass-loss data were treated kinetically with the aid of a computer program in terms of the most commonly proposed models found in [13–18]. The linearity of the kinetic plots was checked in terms of the correlation coefficients (r) and the standard deviations (s) to determine the kinetic model and the Arrhenius parameters.

Fig. 2 shows the typical fraction decomposition reactions (α) versus time (t) curves at different temperatures for the compound $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$. A satisfactorily linear relationship is observed between α and t. Kinetic obedience was determined by plotting various kinetic functions $G(\alpha)$ versus t [13–18], according to

$$G(\alpha) = kt, \tag{1}$$

where k is the apparent rate constant. The best fitting was found, as suggested by the shape of the α versus t curves, with the one-dimensional phase-boundary-controlled model (R_1) within the range $0.15 \leq \alpha \leq 0.95$ as shown in Fig. 3 for the complex $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$; this is in agreement with the work of Tanaka–Koga [19] who studied the kinetics of thermal decomposition of the melted composition of NH_4NO_3 and found this model to be more adapted to the experimental data. These results are confirmed by Dollimore [20], who mentions the equation of this model as one of the equations that describes the thermal decomposition processes in the liquid phase. Table 3 shows the k values obtained according the R_1 model for the cadmium chelates. The temperature dependence of k was derived using the Arrhenius plots, the adjustment can be seen in Fig. 4 for the complex $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$. The calculated values for the kinetic parameters are listed in Table 4.

The kinetics of the thermal decomposition of $Cd(S_2CNR_2)_2$ complexes was also studied using the non-isothermal heating method at two different heating rates, 5 and 10 K min^{-1}, using the Coats–Redfern [11] equation and the R_1 model determined in the isothermal heating experiments, as listed in Table 5, the adjustments are presented in Figs. 5 and 6 for the complex $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$. Table 5 shows that although the same order in the activation apparent energy values for the complexes also observed, as found in the thermogravimetric isothermal experiments, the activation apparent energies from non-isothermal experiments are systematically higher than those obtained from the isothermal method. A similar behaviour was also observed by Ghosh and Jere [21]. These authors attributed these differences to the kinetic compensation effect (KCE). In fact we observed a good linear correlation between $\ln A$ and E, according to

$$\ln A = a + bE, \tag{2}$$

where A is the pre-exponential factor, E the activation apparent energy and a and b are the constants to be

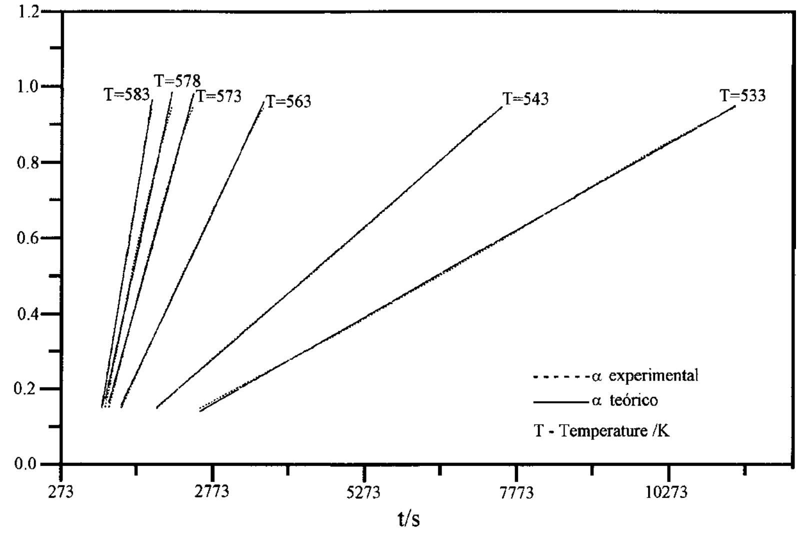

Fig. 3. Decomposition like the R_1 model for $Cd(S_2CNPr^n_2)_2$.

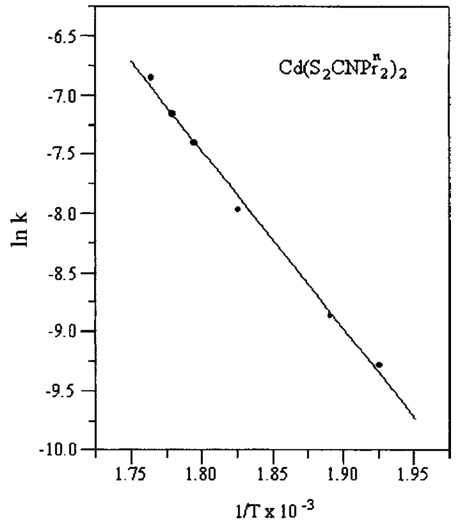

Fig. 4. Plot of the equation of Arrhenius.

evaluated. Table 6 shows the values for a, b and the linear regression coefficients (r) calculated using expression (2).

The values of the activation apparent energy for the cadmium complexes suggest the same order of thermal stability observed in the thermogravimetric curves,

$$Cd(S_2CNBu^n_2)_2 > Cd(S_2CNPr^n_2)_2 > Cd(S_2CNBu^i_2)_2 > Cd(S_2CNEt_2)_2,$$

in agreement with Magee and Hill [22], which proposed

Table 3
Constant rates according to R_1 model

Complexes	Temperatures (K)	Parameter		
		$k\times10^4(s^{-1})$	r	$s\times10^3$
$Cd(S_2CNEt_2)_2$	533	1.30	0.9999	3.5
	543	1.95	0.9997	5.7
	533	3.08	0.9994	7.9
	563	4.94	0.9997	5.8
	573	8.96	0.9991	10.6
	578	10.8	0.9990	11.6
$Cd(S_2CNPr^n_2)_2$	533	0.921	0.9999	3.5
	543	1.41	0.9999	2.22
	563	3.48	0.9998	4.22
	573	6.10	0.9991	10.1
	578	7.74	0.9979	15.3
	583	10.5	0.9997	5.79
$Cd(S_2CNBu^n_2)_2$	538	0.77	0.9996	6.58
	543	1.01	0.9996	6.7
	558	2.13	0.9998	4.1
	578	5.35	0.9984	13.5
	583	6.80	0.9992	9.6
	588	9.17	0.9989	11.5
$Cd(S_2CNBu^i_2)_2$	528	0.661	0.9999	2.24
	543	1.36	0.9999	1.52
	553	2.15	0.9998	4.32
	563	3.51	0.9997	5.31
	573	6.02	0.9998	4.16
	578	7.50	0.9998	4.17

r=linear correlation coefficient; s=standard deviation.

Table 4
Calculated kinetic parameters using the Arrhenius equation $k=A\exp(-E/RT)$

Parameters	Complexes			
	$Cd(S_2CNEt_2)_2$	$Cd(S_2CNPr^n_2)_2$	$Cd(S_2CNBu^n_2)_2$	$Cd(S_2CNBu^i_2)_2$
E (kJ mol^{-1})	123.4	124.8	127.8	123.9
A (s^{-1})	1.5E+08	1.5E+08	1.95E+08	1.1E+08
r	0.9970	0.9974	0.9996	0.9990

Table 5
Kinetic parameters determined using dynamic thermogravimetric method of Coats–Redfern's equation

Parameters	Heating rate (K min^{-1})	Complexes			
		$Cd(S_2CNEt_2)_2$	$Cd(S_2CNPr^n_2)_2$	$Cd(S_2CNBu^n_2)_2$	$Cd(S_2CNBu^i_2)_2$
E (kJ mol^{-1})	5	138.6	142.5	148.6	139.2
A (s^{-1})		4.28E+09	8.31E+09	1.51E+10	3.41E+09
r		0.9988	0.9996	0.9989	0.9980
E (kJ mol^{-1})	10	142.7	152.5	163.1	144.3
A (s^{-1})		1.14E+10	6.80E+10	4.31E+11	1.15E+10
r		0.9979	0.9995	0.9982	0.9997

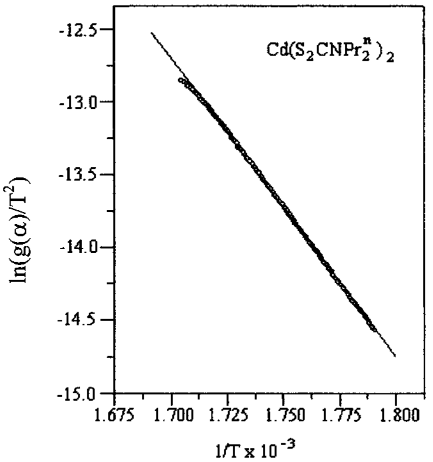

Fig. 5. Plot of the equation of Coats–Redfern, with a heating rate of 5 K min^{-1}.

a correlation between the thermal stability suggested by the TG curves and the calculated activation apparent energies.

4. Conclusions

The thermal decomposition of the solid bis(dialkyldithiocarbamate) Cd(II) complexes, in nitrogen atmosphere, occurs in a single stage, in the liquid phase, after melting in temperatures significantly lower than the unstable thermal temperature ranges, according to the scheme

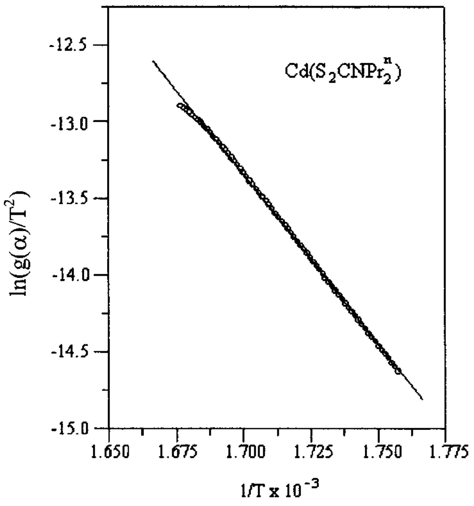

Fig. 6. Plot of the equation of Coats–Redfern, with a heating rate of 10 K min^{-1}.

$$Cd(S_2CNR_2)_2(cr) \rightarrow Cd(S_2CNR_2)_2(l) \rightarrow S_2CNR_2(g) + SCNR_2(g) + SCd(cr).$$

Table 6
KCE constants calculated according to expression (2), using the values of A and E obtained from the TG isothermal and dynamic experiments

Complexes	$-a$	b	r
$Cd(S_2CNEt_2)_2$	8.84	0.224	0.9998
$Cd(S_2CNPr^n_2)_2$	8.90	0.222	0.9997
$Cd(S_2CNBu^n_2)_2$	8.79	0.218	0.9996
$Cd(S_2CNBu^i_2)_2$	9.34	0.225	0.9999

The kinetic that better model was adjusted to the experimental data, using the method isothermal was one-dimensional phase-boundary controlled model (R_1) within the range $0.15\leq\alpha\leq0.95$.

The thermal analysis data showed that all the four $Cd(S_2CNR_2)_2$ chelates decompose in a similar way in the temperature range 528–588 K, according to the same kinetic model. This result is not surprising owing to the fact that the structural modification was introduced in the site far removed from the coordination sphere.

The thermal stability of $Cd(S_2CNR_2)_2$ complexes, according the TG curves follows the sequence: $Cd(S_2CNBu^n_2)_2 > Cd(S_2CNPr^n_2)_2 > Cd(S_2CNBu^i_2)_2 > Cd(S_2CNEt_2)_2$. The same order of thermal stability is suggested by the calculated activation apparent energies in both the isothermal and non-isothermal experiments.

The values of the energy of activation apparently estimated by dynamic method are larger than that estimated by isothermal, however obeyed the effect of the kinetic compensation.

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