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KINETIC ANALYSIS OF THE DECOMPOSITION OF CHELATES OF DI-ALKYLDITHIOCARBAMATE OF Cd(II)

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Abstract

The thermal decomposition kinetics of the solid complexes $Cd(S_2CNR_2)_2$, where $R=C_2H_5$, n-C_3H_7, n-C_4H_9 or *iso*-C_4H_9, was studied by using isothermal and non-isothermal thermogravimetry. The superimposed TG/DTG/DSC curves revealed that thermal decomposition reactions occur in the liquid phase. The kinetic model that best fitted the experimental isothermal TG data was the one-dimensional phase-boundary reaction-controlled process R_1. The thermal analysis data suggested the thermal stability sequence $Cd(S_2CNBu^n_2)_2>Cd(S_2CNPr^n_2)_2>Cd(S_2CNBu^i_2)_2>Cd(S_2CNEt_2)_2$, which accords with the sequence of stability of the apparent activation energies.

Keywords: cadmium, dialkyldithiocarbamate, kinetics, thermal decomposition, thermogravimetry

Introduction

Interest in the chemistry of the dithiocarbamates seems not only from the analytical value of these compounds, but also from their industrial applicability [1–5]. The thermochemistry of metal dithiocarbamates has been widely studied in recent years [6–9], but little is known about their thermal decomposition kinetics. Additionally, these solid metal complexes have been found to decompose in the liquid phase in a range of temperature far from their melting points, and consequently it is expected that the overall reactions should not be complicated by partial liquefaction occurring in a confined and restricted zone, as usually observed.

In the present work, we report on a study of the kinetics of thermal decomposition of the 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 (B^n) or *iso*-C_4H_9 (B^i), with the use of isothermal and non-isothermal heating methods.

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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.

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-*iso*-butylamine (Merck) and carbon disulfide (Merck) were purified and distilled, respectively. The cadmium(II) chloride was purified and dried in vacuo.

Preparations

The compounds $Cd(S_2CNR_2)_2$, where (R=ethyl, *n*-propyl, *n*-butyl or *iso*-butyl) were prepared by slow addition of a solution of dialkylammonium dialkyldithiocarbamate $H_2NR_2CNR_2$ in acetone to a stirred solution of $CdCl_2$ in acetone in 1:2 molar proportion. After filtration, the crystals formed were washed with petroleum ether, 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. Microanalysis results for carbon, hydrogen, nitrogen and cadmium were within experimental error of the values expected from the established formulae.

Thermal measurements

Thermogravimetric curves were obtained with a Shimadzu model TGA-50 thermobalance, under a 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 ranges in which the thermogravimetric isothermal curves were recorded were 260–305°C for $Cd(S_2CNEt_2)_2$, 260–310°C for $Cd(S_2CNPr^n_2)_2$, 265–315°C for $Cd(S_2CNBu^n_2)_2$, and 255–305°C for $Cd(S_2CNBu^i_2)$, and the heating rate was 5 or 10 K min^{-1} for non-isothermal experiments.

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

The kinetic parameters in the dynamic heating method were determined according to the Coats-Redfern [10] equation, using the thermal decomposition model suggested by the data obtained in the isothermal heating experiments.

Other measurements

The melting temperatures for all compounds were determined by means of a Microquimica model MQAPF-301 apparatus. Microanalyses for carbon, hydrogen and nitrogen were performed with a Perkin Elmer Elemental Analyser model PE-24000, and cadmium was analysed in a GBC Atomic Absorption Spectrophotometer model 908-AA. Infrared spectra were recorded in KBr pellets, in the region 4000–200 cm^{-1}, us-

Table 1 Melting points (T_M), mass percentage analyses of C, H, N (%) and atomic absorption of Cd (%) and C–N and C–S stretching wavenumbers (cm^{-1})

Complexes	T_M/°C	Calculated				Experimental				Bands	
		C	H	N	Cd	C	H	N	Cd	νC=N	νC=S
$Cd(S_2CNEt_2)_2$	250	29.37	4.93	6.85	27.48	29.02	4.87	6.84	25.89	1496.59	1073.31
$Cd(S_2CNPr^n_2)_2$	151	36.15	6.06	6.02	24.17	36.20	6.10	5.85	23.98	1495.73	1100.13
$Cd(S_2CNBu^n_2)_2$	137	41.48	6.95	5.37	21.56	41.51	6.82	5.61	20.85	1495.78	1093.17
$Cd(S_2CNBu^i_2)_2$	164	41.48	6.95	5.37	21.56	41.76	6.74	5.42	20.93	1486.66	1090.84

ing a Bomem model MB-102 series FTIR spectrophotometer, while the mass spectra of the ligand and chelates were recorded on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV, 523 K.

Results and discussion

The nitrogen, carbon, hydrogen and cadmium elemental analysis results on the complexes [$Cd(S_2CNR_2)_2$], with R=C_2H_5, n-C_3H_7, n-C_4H_9, and *iso*-C_4H_9, are in good agreement with the values expected for the compounds, as shown in Table 1. The melting temperatures observed are consistent with the purity of these compounds, as indicated in Table 1. The mode of coordination of the dialkyldithocarbamate and the definite melting points suggest the existence of very stable compounds. However, when the melted sample was cooled and then heated again, the previous melting-point interval was not reproduced. The νCN band assumed a double-band character, which is reflected in the appearance of a stretching band shifted to higher frequency. For all complexes, this band frequency was higher than that for the respective ligand. On the other hand, a decrease in the νCS stretching band was observed and an isolated band near 1000 cm^{-1} indicated that the ligand is bonded to the metal in a bidentate manner [6–9, 11]. 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 sequence of stability:

$$Cd(S_2CNEt_2)_2>Cd(S_2CNPr_2^n)_2>Cd(S_2CNBu_2^n)_2>Cd(S_2CNBu_2^i)_2$$

The intensities of the peaks observed were 13.43, 10.82, 6.65 and 5.00%, respectively.

Figure 1 shows typical TG(DTG) and DSC curves for the thermal behaviour of $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$. As shown by the DSC curve, the thermal decomposition begins at a temperature significantly higher (~90°C) than the melting point of the compound and hence in the liquid phase, in a single-stage process, as suggested by the TG/DTG curves. The same behaviour was also found for the three other complexes, as shown in Table 2. The thermal decomposition data obtained in the dynamic TG experiments, listed in Table 2, together with those obtained from DSC measurements, are in good

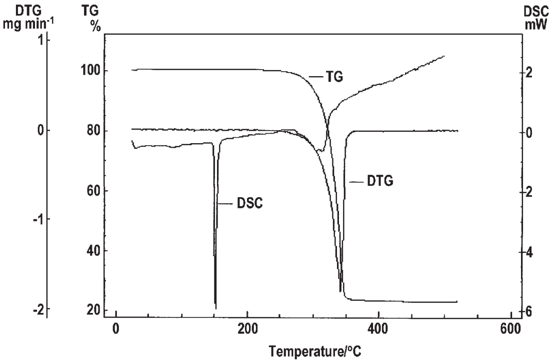

Fig. 1 Superimposed TG/DTG/DSC curves of the complex $Cd(S_2CNPr_2^n)_2$

agreement with the following scheme for the thermal decomposition reactions for the Cd(II) bis(dialkyldithiocarbamates):

$$\mathrm{Cd(S_2CNR_2)_2(cr)} \rightarrow \mathrm{Cd(S_2CNR_2)_2(1)} \rightarrow \mathrm{S_2CNR_2(g){+}SCNR_2(g){+}SCd(cr)}$$

After melting, the cadmium complexes decompose in a single-stage process by partial loss of the ligands, leaving cadmium sulphide as residue. The isothermal mass-loss data were treated kinetically with the aid of a computer program in terms of the most usual proposed models to be found in the literature [12–17]. 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.

Table 2 Thermal decomposition results after thermogravimetric experiments

Complexes	Experimental conditions	Stage	Reaction interval	Mass loss/%
$Cd(S_2CNEt_2)_2$	(1)	1	225–340	78.6
	residue		>420	21.4
	(2)	1	233–355	76.8
	residue		>420	23.2
$Cd(S_2CNPr^n_2)_2$	(1)	1	232–345	76.0
	residue		>420	24.0
	(2)	1	247–361	76.3
	residue		>420	23.7
$Cd(S_2CNBu^n_2)_2$	(1)	1	243–353	75.1
	residue		>420	24.9
	(2)	1	253–363	77.0
	residue		>420	23.0
$Cd(S_2CNBu^i_2)_2$	(1)	1	230–343	85.4
	residue		>420	14.6
	(2)	1	236–360	83.7
	residue		>420	16.3

(1) sample mass around 5 mg, heating rate 5 K min^{-1}, nitrogen flow rate 33.3 $cm^3\ s^{-1}$
(2) sample mass around 5 mg, heating rate 10 K min^{-1}, nitrogen flow rate 33.3 $cm^3\ s^{-1}$

Figure 2 shows typical fraction decomposition (α) *vs*. 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 $G(\alpha)$ *vs*. *t*, according to

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

where *k* is the apparent rate constant.

As suggested by the shapes of the α *vs*. *t* curves, the best fit was found for the one-dimensional phase-boundary-controlled model (R_1) within the range

$0.15 \leq \alpha \leq 0.95$, as revealed by Fig. 3 for the complex $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$. This is in agreement with the work of Koga and Tanaka [18], who studied the kinetics of thermal decomposition of the melted composition NH_4NO_3 and found this model to fit most closely to the experimental data. These results are confirmed by the literature [19], which mentions the equation of this model as one of the equations that describes thermal decomposition processes in the liquid phase. Table 3 presents the k values obtained according to the R_1 model for the cadmium chelates. The temperature dependence of k was derived by using the Arrhenius plots. The fit for the complex $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$ can be seen in Fig. 4. The calculated values for the kinetic parameters are listed in Table 4.

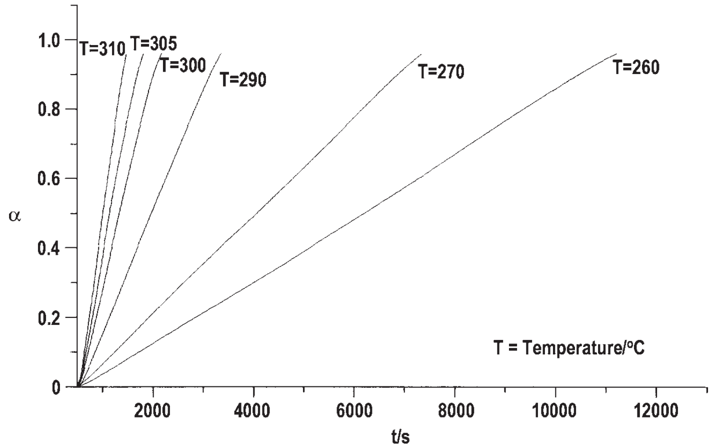

Fig. 2 Isothermal decomposition of $Cd(S_2CNPr_2^n)_2$

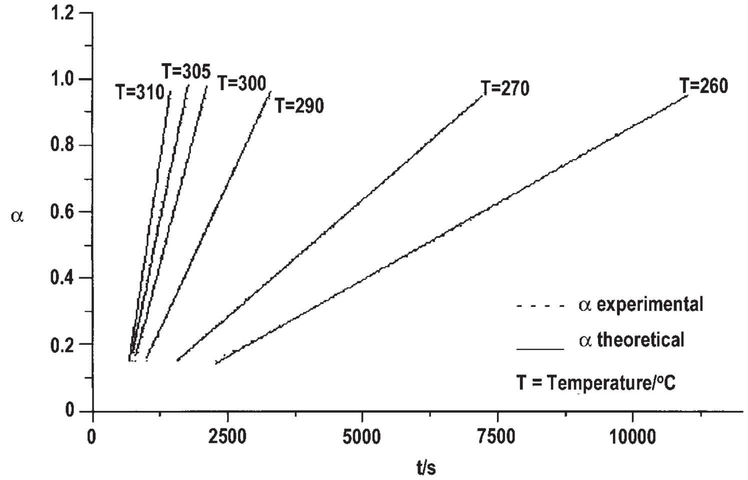

Fig. 3 Decomposition via the R_1 model for $Cd(S_2CNPr_2^n)_2$

Table 3 Constant rates according to the R_1 model

Complex	Parameter	Temperatures/°C					
$Cd(S_2CNEt_2)_2$		260	270	280	290	300	305
	$k\cdot 10^4/s^{-1}$	1.30	1.95	3.08	4.94	8.96	10.8
	r	0.9999	0.9997	0.9994	0.9997	0.9991	0.9990
	$s\cdot 10^3$	3.5	5.7	7.9	5.8	10.6	11.6
$Cd(S_2CNPr^n_2)_2$		260	270	290	300	305	310
	$k\cdot 10^4/s^{-1}$	0.921	1.41	3.48	6.10	7.74	10.5
	r	0.9999	0.9999	0.9998	0.9991	0.9979	0.9997
	$s\cdot 10^3$	3.5	2.22	4.22	10.1	15.3	5.79
$Cd(S_2CNBu^n_2)_2$		265	270	285	305	310	315
	$k\cdot 10^4/s^{-1}$	0.77	1.01	2.13	5.35	6.80	9.17
	r	0.9996	0.9996	0.9998	0.9984	0.9992	0.9989
	$s\cdot 10^3$	6.58	6.7	4.1	13.5	9.6	11.5
$Cd(S_2CNBu^i_2)_2$		255	270	280	290	300	305
	$k\cdot 10^4/s^{-1}$	0.661	1.36	2.15	3.51	6.02	7.50
	r	0.9999	0.9999	0.9998	0.9997	0.9998	0.9998
	$s\cdot 10^3$	2.24	1.52	4.32	5.31	4.16	4.71

r – linear correlation coefficient
s – standard deviation

Table 4 Kinetic parameters calculated by using the Arrhenius equation $k=Ae(-E/RT)$

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

The kinetics of thermal decomposition of the complexes $Cd(S_2CNR_2)_2$ was also studied by using the non-isothermal heating method at two different heating rates, 5 and 10 K min^{-1}, via the Coats-Redfern [10] equation and the R_1 model determined in the isothermal heating experiments, as listed in Table 5. The fit for the complex $Cd[S_2CN(n\text{-}C_3H_7)_2]_2$ is presented in Figs 5 and 6. Table 5 shows too that, although the same sequence of apparent activation energy values is observed for the complexes as found in the thermogravimetric isothermal experiments, the apparent activation energies from non-isothermal experiments are systematically higher than those obtained from the isothermal method. Similar behaviour was observed by Ghosh and Jere [20]. Those 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

$$\ln A = a + bE \qquad (2)$$

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

Table 6 shows the values for a and b and the linear regression coefficients (r) calculated by using Eq. (2).

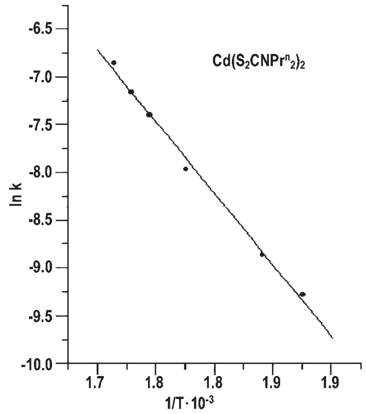

Fig. 4 Plot of the Arrhenius equation

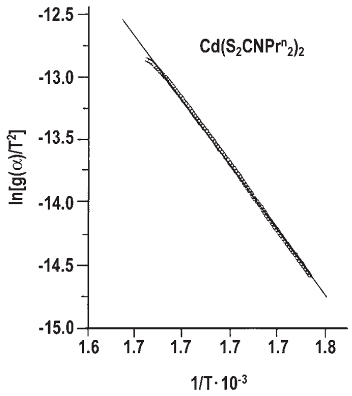

Fig. 5 Plot of the Coats-Redfern equation with a heating rate of 5 K min^{-1}

The values of the apparent activation energy for the cadmium complexes suggest the same sequence of thermal stability as observed in the thermogravimetric curves:

$$Cd(S_2CNBu_2^n)_2 > Cd(S_2CNPr_2^n)_2 > Cd(S_2CNBu_2^i)_2 > Cd(S_2CNEt_2)_2$$

in agreement with Magee and Hill [21], who proposed a correlation between the thermal stability suggested by the TG curves and the calculated apparent activation energies.

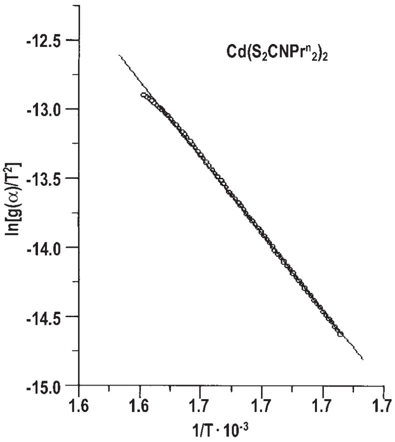

Fig. 6 Plot of the Coats-Redfern equation with a heating rate of 10 K min^{-1}

Table 5 Kinetic parameters determined by using the dynamic thermogravimetric method of Coats-Redfern

Parameter	Heating rate/ K min^{-1}	Complexes, $Cd(S_2CNR_2)_2$			
		R=Et	R=Pr^n	R=Bu^n	R=Bu^i
E/kJ mol^{-1}		138.6	142.5	148.6	139.2
A/s^{-1}	5	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}		142.7	152.5	163.1	144.3
A/s^{-1}	10	1.14E+10	6.80E+10	4.31+11	1.15+10
R		0.9979	0.9995	0.9982	0.9997

Table 6 KCE constants calculated according to expression (2), using the values of A and E obtained in 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

Conclusions

The thermal decomposition of the solid bis(dialkyldithiocarbamate) complexes of Cd(II) in a nitrogen atmosphere occurs in a single-stage, in the liquid phase, after melting at temperatures significantly lower than the temperature range of thermal instability.

The kinetic model that best fitted to the experimental data, using the isothermal method, was the one-dimensional phase-boundary-controlled model (R_1) within the range $0.15\leq \alpha \leq 0.95$.

The thermal analysis data showed that all four chelates $Cd(S_2CNR_2)_2$ decompose in a similar way in the temperature range 255–315°C, according to the same kinetic model. This result is not surprising in view of the fact that the structural modification involves sites far removed from the coordination sphere.

According to the TG curves, the thermal stabilities of the complexes $Cd(S_2CNR_2)_2$ follow 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 sequence of thermal stability is suggested by the calculated apparent activation energies in both isothermal and non-isothermal experiments.The values of the apparent energy of activation, estimated by the dynamic method, are larger than those estimated by the isothermal method, but the KCE is obeyed.

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