

KINETIC ANALYSIS OF THE THERMAL DECOMPOSITION OF DIALKYLDITHIO-CARBAMATES CHELATES OF INDIUM(III)

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Abstract

The kinetics of thermal decomposition of solid $\text{In}(\text{S}_2\text{CNR}_2)_3$ complexes, ($R=\text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$ and $i\text{-C}_4\text{H}_9$), has been studied using isothermal and non-isothermal thermogravimetry. Superimposed TG/DTG/DSC curves show that thermal decomposition reactions occur in the liquid phase, except for the $\text{In}(\text{S}_2\text{CNMe}_2)_3$ and $\text{In}(\text{S}_2\text{CNPr}_2)_3$ compounds.

Keywords: dialkyldithiocarbamates, indium, kinetics, thermogravimetry

Introduction

Studies concerning the kinetics of thermal decomposition of dialkyldithiocarbamates metallic complexes are scant in literature. Recently, Machado *et al.* [1] and Rangel *et al.* [2] have studied the kinetics of isothermal and non-isothermal decomposition of cadmium(II) and palladium(II) complexes, in both these studies TG and DSC techniques were used. These authors showed that there is no direct relationship between apparent activation energy and the thermal stability of the complexes.

In the present work the kinetics of the thermal decomposition of Indium(III) dialkyldithiocarbamates, $\text{In}(\text{S}_2\text{CNR}_2)_3$, with $R=\text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, or $i\text{-C}_4\text{H}_9$, using isothermal and non-isothermal heating methods was studied.

Experimental

In(III) dialkyldithiocarbamates complexes were synthesized from direct reaction of InCl_3 with the various dialkyldithiocarbamate dialkylammonium compounds in water, in 1:3 molar proportion [3, 4]. After filtration, the crystals were recrystallized in acetone and dried in vacuum.

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Characterization measurements

The melting points were determined using a Microquimica (model MQAPF-301) apparatus. Infrared spectra were recorded in the range 4000–200 cm^{-1} , using a BOMEM (model MB-102) FTIR spectrophotometer; mass spectra of the ligands and chelates were obtained using a Hewlett–Packard (model 5988A) spectrometer, with an ionization energy of 70 eV, at 523 K. The thermal decomposition residues were analysed by X-ray powder diffraction, using an X-ray SIEMENS (model D-5000) diffractometer.

Thermal measurements

Thermogravimetric curves were obtained using a Shimadzu (model TGA-50) thermobalance, under nitrogen atmosphere. The carrier gas flow was always 0.83 mL s^{-1} and the sample masses were 5.0 ± 0.5 mg. For the non-isothermal experiments, three different heating rates were used: 5, 10 and $15^\circ\text{C min}^{-1}$.

DSC curves were obtained under nitrogen atmosphere, using a Shimadzu (model DSC-50) differential scanning calorimeter, with heating rate of $10^\circ\text{C min}^{-1}$.

Results and discussion

The elemental analysis and melting points are in good agreement with the expected values for all compounds. After complex formation, the νCN band assumes a doublet character reflected in the presence of a stretching band shifted to higher frequency, in comparison with the respective free 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 bound to the metal in a bidentate way [5].

The mass spectra of the complexes indicated the presence of the parent ions, except for $\text{In}(\text{S}_2\text{CNPr}_2^i)_3$, with the following stability order: $\text{In}(\text{S}_2\text{CNPr}_2^n)_3 > \text{In}(\text{S}_2(\text{CNMe}_2)_3) > \text{In}(\text{S}_2\text{CNBu}_2^i)_3 > \text{In}(\text{S}_2\text{CNBu}_2^n)_3 > \text{In}(\text{S}_2\text{CNEt}_2)_3 > \text{In}(\text{S}_2\text{CNPr}_2^i)_3$.

The thermogravimetric curves of the complexes presented a very similar behavior. The complexes show one definite step of mass loss, attributed to the ligand loss. The following order of thermal stability is observed: $\text{In}(\text{S}_2(\text{CNMe}_2)_3) > \text{In}(\text{S}_2\text{CNBu}_2^n)_3 > \text{In}(\text{S}_2\text{CNEt}_2)_3 > \text{In}(\text{S}_2\text{CNPr}_2^n)_3 > \text{In}(\text{S}_2\text{CNPr}_2^i)_3 \sim \text{In}(\text{S}_2\text{CNBu}_2^i)_3$.

X-ray diffraction analysis of the thermal decomposition residues showed that, except for the $\text{In}(\text{S}_2\text{CNBu}_2^n)_3$ complex, the complexes that decompose in the liquid phase, $\text{In}(\text{S}_2\text{CNEt}_2)_3$, $\text{In}(\text{S}_2\text{CNPr}_2^n)_3$, $\text{In}(\text{S}_2\text{CNBu}_2^n)_3$ and $\text{In}(\text{S}_2\text{CNBu}_2^i)_3$, presented In^0 as residue. The complexes that decompose in the solid phase, $\text{In}(\text{S}_2(\text{CNMe}_2)_3)$, $\text{In}(\text{S}_2\text{CNPr}_2^i)_3$ and $\text{In}(\text{S}_2\text{CNBu}_2^i)_3$, had In_2S_2 as residue.

Isothermal decomposition

The experimental data for isothermal decomposition were evaluated with the aid of a linear regression program for the most commonly proposed models [6–8], using the relationship:

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

where k_0 is the induction period.

The temperature ranges for isothermal experiments were obtained from TG curves for each complex. Experimental data were evaluated in terms of decomposed fraction (α) as a function of time (t). Experimental temperatures for each complex were: 323, 329, 332, 335 and 338°C for $\text{In}(\text{S}_2\text{CNMe}_2)_3$; 283, 290, 293, 297 and 305°C for $\text{In}(\text{S}_2\text{CNEt}_2)_3$; 285, 290, 295, 300 and 303°C for $\text{In}(\text{S}_2\text{CNPr}_2^{\text{n}})_3$; 267, 270, 273, 282 and 281°C for $\text{In}(\text{S}_2\text{CNPr}_2^{\text{i}})_3$; 297, 303, 309, 312 and 315°C for $\text{In}(\text{S}_2\text{CNBu}_2^{\text{n}})_3$ and 283, 286, 289, 292 and 295°C for $\text{In}(\text{S}_2\text{CNBu}_2^{\text{i}})_3$.

For $\text{In}(\text{S}_2\text{CNEt}_2)_3$, $\text{In}(\text{S}_2\text{CNPr}_2^{\text{n}})_3$, $\text{In}(\text{S}_2\text{CNBu}_2^{\text{n}})_3$ and $\text{In}(\text{S}_2\text{CNBu}_2^{\text{i}})_3$ chelates, a linear relationship between α and t was observed, in the range $0.1 \leq \alpha \leq 0.9$. The same behavior was not observed for $\text{In}(\text{S}_2\text{CNMe}_2)_3$ and $\text{In}(\text{S}_2\text{CNPr}_2^{\text{i}})_3$. For these two chelates α vs. t curves presented a sigmoidal shape with a significant induction period. This behavior could be due to the beginning of the decomposition already in the solid phase, which opposite to the behavior observed for other chelates, the decomposition of which occurs completely in liquid phase.

Using the linear correlation coefficients (r) or the standard deviations (s), as criterion of analysis, the most appropriated model to describe the experimental results for the complexes $\text{In}(\text{S}_2\text{CNR}_2)_3$ (with $R = \text{Et}, \text{Pr}^{\text{n}}, \text{Bu}^{\text{n}}$ and Bu^{i}) was the phase-boundary reaction, R1. The A3 model seems to be equally good to fit the experimental data for $\text{In}(\text{S}_2\text{CNBu}_2^{\text{n}})_3$. For the complexes with $R = \text{Me}$ and Pr^{i} , the model that best adjusted to the experimental data was the nucleation and nucleus growth models, A3 and A4. For all fittings, linear correlation coefficients (r) were equal or better than 0.998, and standard deviations (s) were in the interval $(0.09-1.6) \cdot 10^{-2}$.

The kinetic parameters were calculated according the Arrhenius equation:

$$k = A \exp(-E/RT) \quad (2)$$

where k – is the rate constant, A – is the pre-exponential factor and E – is the apparent activation energy. The results are summarized in Table 1.

Non-isothermal decomposition

The kinetics of thermal decomposition of the $\text{In}(\text{S}_2\text{CNR}_2)_3$ chelates was also studied using the non-isothermal heating method, with heating rates of 5, 10 and 15°C min⁻¹, according to the expression proposed by Coats and Redfern [9]:

$$\ln[g(\alpha)/T^2] = \ln[AR/\phi E] - E/RT \quad (3)$$

where T – the absolute temperature, E – the apparent activation energy, A – the pre-exponential factor, R – the gas constant, ϕ – the heating rate and $g(\alpha)$ – the kinetic model. The results of experimental data treatment are presented in Table 2.

In spite of the known limitations of the non-isothermal technique in the study of thermal decomposition kinetics [10], these results are in reasonable agreement with the isothermal ones, particularly in the more appropriate models to fit the experimental data.

Table 1 Kinetic parameters calculated according to the Arrhenius equation, for the isothermal TG experiments

Model	Parameter	Complexes					
		In(S ₂ CNMe ₂) ₃	In(S ₂ CNEt ₂) ₃	In(S ₂ CNPr ⁿ) ₃	In(S ₂ CNPr ⁱ) ₃	In(S ₂ CNBu ⁿ) ₃	In(S ₂ CNBu ⁱ) ₃
R1	<i>E</i> /kJ mol ⁻¹		147.01	188.01		138.24	132.69
	<i>A</i> /s ⁻¹		4.29E+09	1.89E+13		5.64E+08	1.40E+08
	<i>r</i>		0.9996	0.9980		0.9992	0.9987
A3	<i>E</i> /kJ mol ⁻¹	181.50			183.78	137.65	
	<i>A</i> /s ⁻¹	3.15E+12			3.04E+14	4.85E+08	
	<i>r</i>	0.9939			0.9991	0.9992	
A4	<i>E</i> /kJ mol ⁻¹	219.46			186.78		
	<i>A</i> /s ⁻¹	5.01E+15			4.78E+14		
	<i>r</i>	0.9924			0.9992		

Table 2 Kinetic parameters determined using non-isothermal TG method, according to the equation of Coats–Redfern [9]

Parameter	φ/°C min ⁻¹	Complexes					
		In(S ₂ CNMe ₂) ₃	In(S ₂ CNEt ₂) ₃	In(S ₂ CNPr ⁿ) ₃	In(S ₂ CNPr ⁱ) ₃	In(S ₂ CNBu ⁿ) ₃	In(S ₂ CNBu ⁱ) ₃
		A4 Model	R1 Model	R1 Model	A2 Model	A2 Model	R1 Model
<i>E</i> /kJ mol ⁻¹	5	183.60	171.02	187.67	200.43	145.50	142.99
<i>A</i> /s ⁻¹		6.14E+12	7.12E+11	1.91E+13	1.40E+16	6.12E+09	1.95E+09
<i>R</i>		0.9956	0.9998	0.9988	0.9945	0.9972	0.9988
<i>E</i> /kJ mol ⁻¹	10	169.63	173.85	179.76	218.19	149.90	148.35
<i>A</i> /s ⁻¹		6.05E+11	1.22E+12	3.75E+12	5.11E+17	1.60E+10	6.09E+09
<i>R</i>		0.9940	0.9996	0.9992	0.9996	0.9983	0.9989
<i>E</i> /kJ mol ⁻¹	15	144.18	178.14	188.16	193.83	147.13	159.92
<i>A</i> /s ⁻¹		5.42E+09	2.84E+12	1.76E+13	2.84E+15	9.27E+09	3.98E+10
<i>R</i>		0.9973	0.9995	0.9985	0.9998	0.9979	0.9988

The kinetic parameters of the complexes $\text{Pd}(\text{S}_2\text{CNR}_2)_2$, $\text{Cd}(\text{S}_2\text{CNR}_2)_2$ and $\text{In}(\text{S}_2\text{CNR}_2)_3$, where $R=\text{Et}$, Pr^n , Bu^n or Bu^i were analysed with the purpose of comparing the thermal behavior of this class of chelates [1, 2]. All complexes decomposed in the liquid phase, after melting, and their experimental data of thermal decomposition were adjusted according to the same phase-boundary reaction model (R1).

The values of apparent activation energy, E , and the pre-exponential factor, A , did not change significantly for these chelates, except for the $\text{In}(\text{S}_2\text{CNPr}_2^i)_3$ complex. This behavior suggests that the mechanism of thermal decomposition for at least a significant number of metal ion complexes of this class of metal complexes is affected neither by the central metal ion nor by the radical.

Conclusions

The In(III) dialkyldithiocarbamate complexes $\text{In}(\text{S}_2\text{CNR}_2)_3$, where $R=\text{Et}$, Pr^n , Bu^n or Bu^i decompose in the liquid phase, after melting, according to the same phase-boundary reaction model, R1. The other two complexes, i. e., $\text{In}(\text{S}_2\text{CNMe}_2)_3$ and $\text{In}(\text{S}_2\text{CNPr}_2^i)_3$, decompose in the solid phase, before melting, according to the nucleus growth controlling process (A3 or A4 models).

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References

- 1 M. C. N. Machado, L. M. Nunes, C. D. Pinheiro, J. C. Machado and A. G. Souza, *Thermochim. Acta*, 328 (1999) 201.
- 2 J. H. G. Rangel, S. F. Oliveira, J. G. P. Espínola and A. G. Souza, *Thermochim. Acta*, 328 (1999) 187.
- 3 A. G. Souza, F. Souza Neto, J. H. Souza, R. O. Macêdo, J. B. L. Oliveira and C. D. Pinheiro, *J. Thermal Anal.*, 49 (1997) 679.
- 4 M. M. Oliveira, G. M. Pessoa, L. C. Carvalho, C. Peppe, A. G. Souza and C. Airoidi, *Thermochim. Acta*, 328 (1999) 223.
- 5 F. Bonati and R. Ugo, *J. Organometal. Chem.*, 10 (1967) 257.
- 6 S. F. Hulbert, *J. Br. Ceram. Soc.*, 6 (1969) 11.
- 7 J. Sestak, V. Satava and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 332.
- 8 M. I. Yoshida, M. M. Braga and J. C. Machado, *Thermochim. Acta*, 237 (1994) 347.
- 9 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 10 J. E. House Jr. and R. P. Ralston, *Thermochim. Acta*, 214 (1993) 255.