Thermochimica Acta, 149 (1989) 331–340
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION KINETICS OF SQUARE-PLANAR d^8 BIS(N-MONOSUBSTITUTED-DITHIOCARBAMATO)METAL(II) COMPLEXES

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(Received 3 January 1989)

ABSTRACT

Thermogravimetric (TG) and derivative thermogravimetric (DTG) studies of $[M(S_2CNHR)_2]$ complexes ($M = Ni$, Pd, Pt; $R = Bu^n$, Cx, Ph) in dynamic nitrogen atmosphere have been performed, to determine their modes of decomposition. All of the complexes showed similar TG profiles. Mass loss considerations at the main decomposition stages indicate conversion of the metal(II) dithiocarbamates to sulphides. Reaction orders in each case were estimated by the shape characteristics of the corresponding DTG curves. Finally, kinetic parameters (energy, entropy of activation and pre-exponential factor) were determined from the TG curves.

INTRODUCTION

Recent results from our laboratory have demonstrated that dithiocarbamates with an electron-withdrawing group and a proton on the nitrogen atom may lose the proton to form dithiocarbimates [1–3]. In particular, our studies have shown [1] that when square-planar bis(N-monosubstituted-dithiocarbamato)platinum(II) and palladium(II) complexes ($[M(S_2CNHR)_2]$) are reacted with excess tertiary phosphine (L), a nucleophilic attack by anionic $RHNCS_2^-$ on a coordinated bidentate dithio ligand can occur, to give the neutral dithiocarbimato complexes $[M(S_2C{=}NR)L_2]$. The mechanism of this reaction has been fully investigated by IEHMO calculations based on the frontier molecular orbital approach of chemical reactivity [4]. Moreover, it has been demonstrated [2,3] that strong bases can also remove a proton on the nitrogen atom to form anionic metal(II) dithiocarbimates. In contrast, reaction between nickel(II) dithiocarbamates and most of the nitrogen- or phosphorus-donor ligands affords five-coordinate $[Ni(S_2CNHR)_2L]$ and/or six-coordinate $[Ni(S_2CNHR)_2L_2]$ adducts, depending on the nature of the ligand used [5,6]. As an extension of our previous work [7–12] on the chemical and electronic properties of the various coordination geometries obtainable within the dithio–acid system, a study of the thermal decomposition of metal(II) *N*-alkyldithiocarbamates was undertaken, in an attempt to provide more evidence for the substantial differences in chemistry exhibited by nickel on the one hand and palladium and platinum on the other. To this end we present here thermoanalytical data (TG and DTG) of some typical d^8 square-planar dithiocarbamates with substituents of varying electronic effects. Interpretation and mathematical analysis of these data, as well as evaluation of order of reaction and the energy and entropy of activation are also given.

EXPERIMENTAL

Preparation of samples

Samples of bis(*N*-alkyldithiocarbamato)metal(II) complexes ($[M(S_2CNHR)_2]$, where M=Ni, Pd, Pt, and R=Bu^n, Cx, Ph) were obtained from the reaction between the metal(II) chloride and the appropriate ammonium dithiocarbamate in dimethylsulfoxide (DMSO) solution [3,8,12]. Recrystallization was carried out by dissolving the solid in an acetone–DMSO mixture and reprecipitating with water (yield 85%). The ammonium *N*-alkyldithiocarbamates were prepared and recrystallized as previously reported [3].

Instruments

The TG and DTG curves were obtained using a DuPont model 99 Thermal Analyser combined with a DuPont model 951 Thermogravimetric Analyser. The measurements were performed using a dynamic nitrogen furnace atmosphere at a flow rate of 60 ml min^{-1} up to 900 °C. The heating rate was 10 °C min^{-1} and the sample sizes ranged in mass from 10 to 12 mg.

RESULTS AND DISCUSSION

Thermal behaviour

All of the complexes were subjected to TG analysis from 0–900 °C in nitrogen. The temperature ranges and percentage mass losses of the decompositions, as well as the temperatures of the greatest rate of decomposition DTG_{max} and the theoretical percentage mass losses are given in Table 1. The thermograms obtained for most of the compounds were very similar in character. All the complexes show two-stage weight loss in their TG/DTG curves in a nitrogen atmosphere. The first weight loss corresponds to the formation of their respective sulphides, while the second is due to decom-

TABLE 1

Thermal decomposition data

Complex	Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss (%)	Evolved moiety	Calculated mass (%)
$[Ni(S_2CNHC_4H_9)_2]$	1	100–250	180, 200sh	74.4	$S_2CNHC_4H_9 + SCNHC_4H_9$	74.43
	2	600–850	–	9.3	S	9.02
	Residue	> 850	–	16.3	Ni^0	16.55
$[Ni(S_2CNHC_6H_{11})_2]$	1	165–250	200	78.4	$S_2CNHC_6H_{11} + SCNHC_6H_{11}$	77.70
	2	600–850	–	7.2	S	7.87
	Residue	> 850	–	14.4	Ni^0	14.43
$[Ni(S_2CNHC_6H_5)_2]$	1	110–250	190	76.0	$S_2CNHC_6H_5 + SCNHC_6H_5$	76.55
	2	600–850	–	8.5	S	8.27
	Residue	> 850	–	15.5	Ni^0	15.18
$[Pd(S_2CNHC_4H_9)_2]$	1	100–400	215	65.0	$S_2CNHC_4H_9 + SCNHC_4H_9$	65.61
	2	600–850	750	8.0	S	7.95
	Residue	> 850	–	26.9	Pd^0	26.44
$[Pd(S_2CNHC_6H_{11})_2]$	1a	100–250	250	38.0	$S_2CNHC_6H_{11}$	38.29
	1b	250–300	265	32.0	$SCNHC_6H_{11}$	31.25
	2	600–850	750	6.4	S	7.05
	Residue	> 850	–	23.6	Pd^0	23.41

TABLE 1 (continued)

Complex	Stage	Temperature range (° C)	DTG_{max} (° C)	Mass loss (%)	Evolved moiety	Calculated mass (%)
$[Pd(S_2CNHC_6H_5)_2]$	1	160–300	225	67.0	$S_2CNHC_6H_5 + SCNHC_6H_5$	68.14
	2	600–850	750	7.5	S	7.37
	Residue	> 850	–	25.0	Pd^0	24.49
$[Pt(S_2CNHC_4H_9)_2]$	1	180–330	210, 315	48.0	$S_2CNHC_4H_9 + SCNHC_4H_9$	53.77
	2	650–850	810	11.0	S + unknown	$6.52 + x$
	Residue	> 850	–	41.0	Pt^0	39.71
$[Pt(S_2CNHC_6H_{11})_2]$	1	100–350	272, 290sh	54.1	$S_2CNHC_6H_{11} + SCNHC_6H_{11}$	58.20
	2	660–850	810	10.3	S + unknown	$5.89 + x$
	Residue	> 850	–	35.6	Pt^0	35.91
$[Pt(S_2CNHC_6H_5)_2]$	1a	160–230	215	32.0	$S_2CNHC_6H_5$	31.36
	1b	230–400	250	22.0	$SCNHC_6H_5$	25.25
	2	650–850	810	9.0	S + unknown	$6.11 + x$
	Residue	> 850	–	37.0	Pt^0	37.28

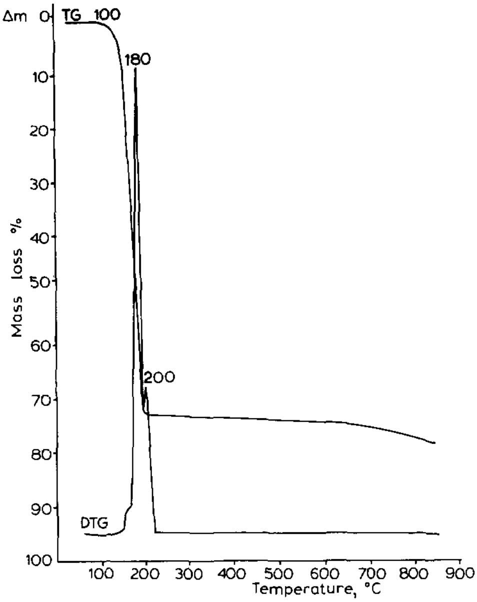

Fig. 1. Thermoanalytical curves of [Ni(S_2CNHBu^n)$_2$] in nitrogen.

position of the sulphides. These intermediates and end products have been confirmed by elemental analysis. It may also be noted here that our observations, based on elemental analysis, on the absence of dehydration peaks in the DTG curves and on the absence of hydroxyl bands in the IR

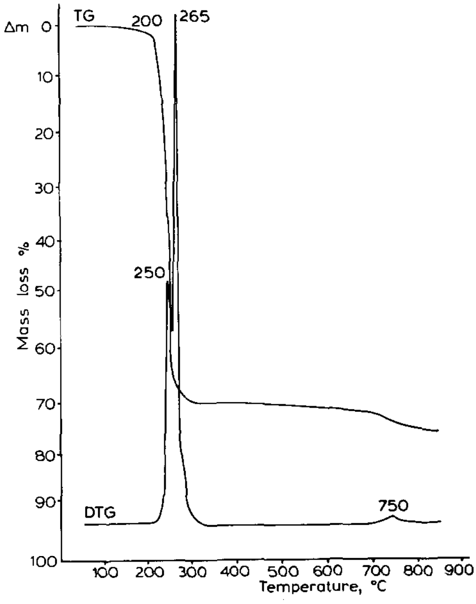

Fig. 2. Thermoanalytical curves of [Pd(S_2CNHCx)$_2$] in nitrogen.

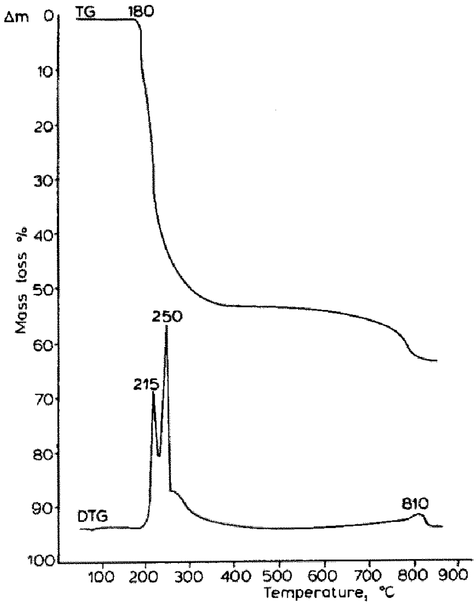

Fig. 3. Thermoanalytical curves of $[Pt(S_2CNHPh)_2$ in nitrogen.

spectra indicate that all the compounds under investigation are anhydrous, which is in agreement with our previous studies [3,12]. The TG and DTG curves of $[Ni(S_2CNHBu^n)_2]$, $[Pd(S_2CNHCx)_2]$ and $[Pt(S_2CNHPh)_2]$ are presented in Figs. 1–3.

In general, decomposition begins between 100 and 180 °C. There then occurs a rapid weight loss in which over 60% of the molecule is lost. It is presumed that metal sulphide is formed at the end of this step, the calculated weight loss showing close agreement with the experimental values. The residue at this stage was also analyzed on sulphur content. Consequently, mass loss at this stage is attributed to the evolved moieties $\{S_2CNHR + SCNHR\}$, according to the following reaction

$$[M(S_2CNHR)_2] \rightarrow MS + \{RHNC(S)S + RHNCS\} \quad (1)$$

In the case of $[Pd(S_2CNHCx)_2]$ and $[Pt(S_2CNHPh)_2]$, however, the decomposition of metal dithiocarbamate to metal sulphide occurs in two substeps. The first weight loss corresponds to the elimination of one dithiocarbamato group. This is followed by the elimination of one thiocarbamoylo group and the formation of metal sulphide after the second weight loss. This main decomposition step is followed by a final weight loss occurring at around 600 °C and leaving a stable residue of the corresponding metal at 850 °C.

Decomposition kinetics

The curves for $[M(S_2CNHR)_2]$ exhibited a characteristic, well-defined and non-overlapping first stage decomposition pattern. This first stage represents the major decomposition step in each case, and mass loss considerations indicated the products to be MS. The first stage was chosen for detailed study. For this purpose the reaction order n was determined from the shape characteristics of the corresponding DTG curves using the following approximation [13–16]

$$X_M \approx 1 - n^{1/(1-n)} \tag{2}$$

where X_M is the conversion at the maximum decomposition rate. Kinetic parameters ($E^\star$, Z) were then evaluated graphically by employing the Coats–Redfern equation [17]

$$\log \frac{\left[1 - \left(\frac{w_\alpha - w}{w_\alpha}\right)^{1-n}\right]}{(1-n)T^2} = \log \frac{ZR}{\Phi E^\star}\left[1 - \frac{2RT}{E^\star}\right] - \frac{E^\star}{2.3R}\frac{1}{T} \tag{3}$$

where w_α is the mass loss at the completion of the first stage reaction, and Φ is the rate of heating (deg min^{-1}). Finally, the entropies of activation $\Delta S^\star$ were obtained from the equation

$$Z = \frac{kT_i}{h}\exp\left(\frac{\Delta S^\star}{R}\right) \tag{4}$$

where k is the Boltzmann constant, h is Planck's constant and T_i is the temperature at the DTG peak.

In studying the decomposition kinetics, it was considered worthwhile to try one other method mentioned in the literature [15,18], using the Horowitz–Metzger equation [19]

$$\log\left[1 - \left(\frac{w_\alpha - w}{w_\alpha}\right)^{1-n}\right] = \log(1-n) + \frac{E^\star}{2.3RT_i^2}\Theta \tag{5}$$

where Θ is the difference between given temperature T and temperature T_i corresponding to maximal decomposition rate (K).

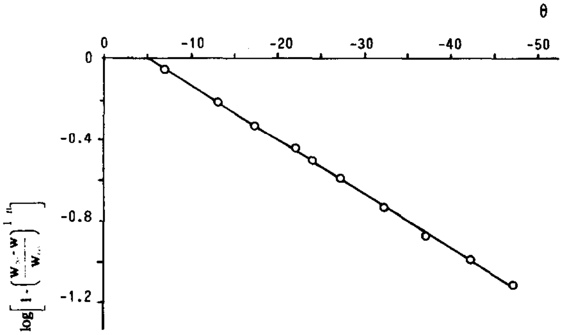

Fig. 4. Horowitz–Metzger plot for [Ni(S$_2$CNHCx)$_2$].

TABLE 2

Kinetic data

Complex [a]	Parameters [b,c]	From Coats–Redfern equation	Form Horowitz–Metzger equation
$[Ni(S_2CNHC_4H_9)_2]$	$E^\star$	183.1	184.9
$w_\alpha = 9.73$ mg	Z	5.85×10^{19}	3.56×10^{19}
$n = 0.915$	$\Delta S^\star$	276.3	272.2
	r	0.992	0.990
$[Ni(S_2CNHC_6H_{11})_2]$	$E^\star$	215.2	240.2
$w_\alpha = 6.13$ mg	Z	4.97×10^{22}	6.69×10^{24}
$n = 0.305$	$\Delta S^\star$	332.1	372.9
	r	0.996	0.990
$[Ni(S_2CNHC_6H_5)_2]$	$E^\star$	244.6	283.6
$w_\alpha = 6.90$ mg	Z	8.87×10^{26}	2.38×10^{30}
$n = 0.281$	$\Delta S^\star$	413.8	479.5
	r	0.995	0.996
$[Pd(S_2CNHC_4H_9)_2]$	$E^\star$	97.0	123.3
$w_\alpha = 10.88$ mg	Z	3.13×10^{8}	1.56×10^{11}
$n = 0.658$	$\Delta S^\star$	59.6	111.3
	r	0.994	0.998
$[Pd(S_2CNHC_6H_{11})_2]$	$E^\star$	151.6	183.1
$w_\alpha = 5.25$ mg	Z	1.19×10^{13}	7.24×10^{15}
$n = 0.335$	$\Delta S^\star$	146.6	200.0
	r	0.997	0.992
$[Pd(S_2CNHC_6H_5)_2]$	$E^\star$	198.6	228.2
$w_\alpha = 3.07$ mg	Z	4.30×10^{19}	1.49×10^{22}
$n = 0.510$	$\Delta S^\star$	2.73.0	321.7
	r	0.993	0.997
$[Pt(S_2CNHC_6H_{11})_2]$	$E^\star$	121.7	153.8
$w_\alpha = 5.58$ mg	Z	8.62×10^{9}	5.41×10^{12}
$n = 0.519$	$\Delta S^\star$	86.3	139.9
	r	0.999	0.995

[a] w_α = total loss of mass for the particular decomposition stage.

[b] Units: $E^\star$, kJ mol^{-1}; Z, s^{-1}; $\Delta S^\star$, J mol^{-1} K^{-1}.

[c] r = correlation coefficient of the linear plot.

Kinetic parameters calculated using the equations given above are summarized in Table 2. Reaction orders and the correlation coefficients r for the corresponding linear plots are also given. Typical curves concerning the application of the above methods are given in Figs. 4–6. All the linear plots were drawn by the least-squares method, and the corresponding correlation coefficients r were also calculated by this means.

However, the orders of reaction for $[Pt(S_2CNHBu^n)_2]$ and $[Pt(S_2CNHPh)_2]$ were found to be 1.918 and 2.013, respectively. In both cases kinetic

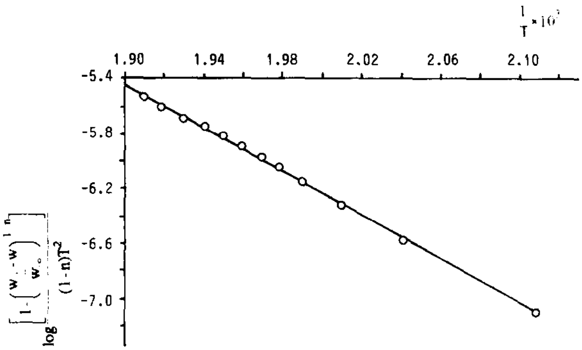

Fig. 5. Coats–Redfern plot for $[Pd(S_2CNHCx)_2]$.

parameters were computer-determined, using the procedures described by Schempf et al. [20], although we had to design our own program. Hence, a least-square polynomial fit of the time–sample weight values to the equation [20,21]

$$w = \sum_{i=0}^{n} C_{(i+1)} t^{i} \tag{6}$$

where n is the desired order polynomial, C the coefficient of the polynomial and t the time, was performed. From the w–t curve thereby generated, the reaction rate constant for any point on the TG curve could be calculated using the equation

$$k = \frac{-\sum_{i=0}^{n-1} [i+1] C_{(i+2)} t^{i}}{\sum_{i=0}^{n} C_{(i+1)} t^{i}} = \frac{\mathrm{d}w/\mathrm{d}t}{w} \tag{7}$$

Finally, the thermodynamic constants were obtained from a least-squares analysis of the values of log k vs. $1000/T$.

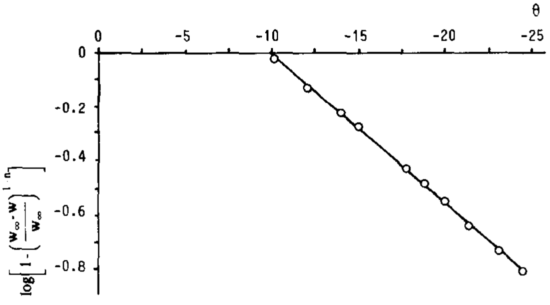

Fig. 6. Horowitz–Metzger plot for $[Pt(S_2CNHCx)_2]$.

On this basis, the activation energies for $[Pt(S_2CNHBu^n)_2]$ and $[Pt(S_2CNHPh)_2]$ were found to be 91.3 and 177.4 kJ mol^{-1}, respectively. The frequency factors were calculated as being equal to 2.94×10^7 and 1.77×10^{17} s^{-1}, and the entropies of activation were found to be 40.6 and 228.0 J mol^{-1} K^{-1}, respectively.

REFERENCES

1 G.A. Katsoulos and C.A. Tsipis, Inorg. Chim. Acta, 84 (1984) 89.
2 C.A. Tsipis, I.J. Meleziadis, D.P. Kessissoglou and G.A. Katsoulos, Inorg. Chim. Acta, 90 (1984) L19.
3 C.C. Hadjikostas, G.A. Katsoulos and S.K. Shakhatreh, Inorg. Chim. Acta, 133 (1987) 129.
4 E.G. Bakalbassis, G.A. Katsoulos and C.A. Tsipis, Inorg. Chem., 26 (1987) 3151.
5 D. Coucouvanis, Progress in Inorganic Chemistry, Vol. 26, Interscience, New York, 1979, p. 301.
6 M.P. Sigalas and C.A. Tsipis, Inorg. Chem., 25 (1986) 1875.
7 G.A. Katsoulos, G.E. Manoussakis and C.A. Tsipis, Inorg. Chim. Acta, 30 (1978) L295.
8 G.A. Katsoulos, G.E. Manoussakis and C.A. Tsipis, Polyhedron, 3 (1984) 735.
9 M. Lalia-Kantouri and G.E. Manoussakis, J. Therm. Anal., 29 (1984) 1151.
10 M. Lalia-Kantouri, A.G. Christofides and G.E. Manoussakis, J. Therm. Anal., 29 (1984) 279.
11 C.A. Tsipis, D.P. Kessissoglou and G.A. Katsoulos, Chim. Chron., 14 (1985) 195.
12 C.C. Hadjikostas, Ph.D. thesis, Aristotle University, Thessaloniki, 1986.
13 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
14 J.H. Flynn and L.A. Wall, J. Res. Nat. Bur. Stand., 70A (1966) 487.
15 J. Sesták, Talanta, 13 (1966) 567.
16 G. Gyulai and E.J. Greenhow, Thermochim. Acta, 6 (1973) 254.
17 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
18 P.M. Madhusudanan, K.K. Mohammed Yusuff and C.G. Ramachandran Nair, J. Therm. Anal., 8 (1975) 31.
19 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
20 J.M. Schempf, F.E. Freeburg, D.J. Roger and F.M. Angeloni, Anal. Chem., 38 (1966) 520.
21 W.W. Wendlandt, Thermochim. Acta, 5 (1973) 225.