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Thermal stability and non-isothermal kinetic study of the decomposition of two coordination compounds of palladium and platinum with ligands derived from thiobenzamide and acetylacetone

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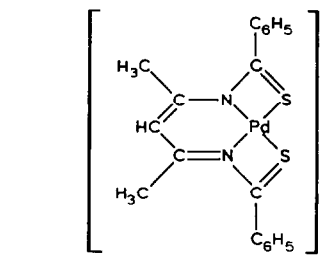
Abstract

The results concerning the thermal behaviour of two coordination compounds synthesised by template condensation are presented. The values of the non-isothermal kinetic parameters have been determined for some of the decomposition steps.

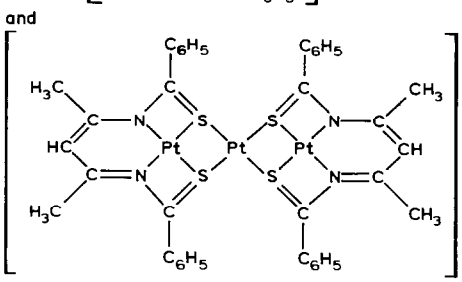
INTRODUCTION

Following our research concerning the thermal decomposition of coordination compounds with ligands derived from thioamides [1], this work deals with the substances



$Cl_2 \cdot H_2O$ or $[PdC_{19}H_{18}N_2S_2]Cl_2 \cdot H_2O$

and



$Cl_6 \cdot 3H_2O$ or $[Pt_3C_{38}H_{36}N_4S_4]Cl_6 \cdot 3H_2O$

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EXPERIMENTAL

The coordination compounds were synthesised according to a method described elsewhere [2].

The heating curves were recorded on an MOM (Budapest) derivatograph, type Paulik–Paulik–Erdey in a static air atmosphere between ambient temperature and 1000 °C, using various heating rates in the range 2.5–10 K min^{-1}.

X-ray diffractograms using chromium K_α radiation were obtained on a Philips P.W.1140 diffractometer. IR spectra were recorded on a SPECORD IR 71, Zeiss Jena spectrophotometer.

In order to evaluate the non-isothermal kinetic parameters, three methods were applied: the Coats–Redfern [3] and the Flynn–Wall [4] for constant heating rate, and the Coats–Redfern method as modified by Urbanovici and Segal [5]. The experimental data were processed automatically using a program written in BASIC language by Dragoe and Segal [6].

The mean sizes of the crystallites were evaluated using Scherrer's formula [7].

RESULTS AND DISCUSSION

The values of the interplanar distances, of the relative intensities and of the mean crystallite sizes for the most intense lines on the diffractograms of compounds 1 and 2 are given in Table 1.

TABLE 1

Primary crystallographic data and mean crystallite size for compounds 1 and 2

Compound	Relative intensity	*d* (Å)	*C* (Å)
1. $[PdC_{19}H_{18}N_2S_2]Cl_2 \cdot H_2O$	100	2.831	459
	71	2.998	
	86	2.483	
	57	2.218	
	57	1.907	
	50	1.749	
	57	1.669	
2. $[Pt_3C_{38}H_{36}N_4S_4]Cl_6 \cdot 3H_2O$	86	5.731	445
	86	5.407	
	50	4.415	
	79	3.864	
	100	3.799	
	64	3.545	
	57	2.809	
	71	2.606	

The decomposition of $[PdC_{19}H_{18}N_2S_2]Cl_2 \cdot H_2O$)

According to the TG curves, the following decomposition steps for this compound are

$$[PdC_{19}H_{18}N_2S_2]Cl_2 \cdot H_2O(s) \xrightarrow{83\,^\circ C} [PdC_{19}H_{18}N_2S_2]Cl_2(s) + H_2O(g) \quad (1)$$

$$[PdC_{19}H_{18}N_2S_2]Cl_2(s) + 5O_2(g) \xrightarrow{240\,^\circ C} [PdC_2H_6N_2S_2]Cl_2(s) + 2C_6H_6(g) + 5CO_2(g) \quad (2)$$

$$[PdC_2H_6N_2S_2]Cl_2(s) + 5.5O_2(g) \xrightarrow{390\,^\circ C} PdS_2(s) + 2CO_2(g) + 2NO_2(g) + Cl_2(g) + 3H_2O(g) \quad (3)$$

$$PdS_2(s) + O_2(g) \xrightarrow{435\,^\circ C} PdS(s) + SO_2(g) \quad (4)$$

$$PdS(s) + O_2(g) \xrightarrow{830\,^\circ C} Pd(s) + SO_2(g) \quad (5)$$

The temperatures written above the arrows correspond to the maximum decomposition rate as shown by the DTG curves.

The existence of $[PdC_2H_6N_2S_2]Cl_2$ as a product of reaction (2) has been confirmed by the IR spectrum which exhibits a band located between 600 and 800 cm^{-1} assigned to the frequency ν(C–S), and a broad band in the range 3350–3500 cm^{-1} corresponding to ν_s(N–H) and ν_{as}(N–H). A similar compound was obtained by the decomposition of the coordination compound between Co(II) and a ligand, formed by template condensation of thiobenzamide and ethylendiamine [1].

The presence of PdS_2, PdS and Pd, as products of reactions (3), (4) and (5), were confirmed by X-ray diffractograms.

The values of the non-isothermal kinetic parameters, reaction order, n, activation energy, E, and pre-exponential factor, A, for reactions (1) and (2) are listed in Tables 2 and 3.

TABLE 2

Values of the non-isothermal kinetic parameters of reaction (1) at $\beta = 2.8$ K min^{-1}

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	2.8	2.24×10^4	2.99×10^{12}
Flynn–Wall	2.7	2.20×10^4	1.16×10^{12}
Modified Coats–Redfern	2.6	2.20×10^4	8.78×10^{11}

TABLE 3

Values of the non-isothermal kinetic parameters of reaction (2) at $\beta = 2.8$ K min^{-1}

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	1.7	2.34×10^4	1.12×10^8
Flynn–Wall	1.7	2.40×10^4	2.68×10^8
Modified Coats–Redfern	1.6	2.30×10^4	6.45×10^7

The relatively low values of the heating rates provide conditions close to isothermal ones, with no heat transfer limitations.

Inspection of the results in Tables 2 and 3 shows quite a good agreement among the values of the non-isothermal kinetic parameters obtained by the three methods applied.

The decomposition of $[Pt_3C_{38}H_{36}N_4S_4]Cl_6 \cdot 3H_2O$

The TG curves of this compound show the following decomposition steps

$$[Pt_3C_{38}H_{36}N_4S_4]Cl_6 \cdot 3H_2O(s) \overset{243°C}{\rightarrow} [Pt_3C_{32}H_{28}N_4S_4]Cl_6(s) + H_2O(g) + O_2(g) + 2C_6H_6(g) \quad (6)$$

$$[Pt_3C_{32}H_{28}N_4S_4]Cl_6(s) + 24.5O_2(g) \overset{330°C}{\rightarrow} PtS \cdot 2NH_3(s) + PtS(s) + PtS_2(s) + 2C_6H_6(g) + 20CO_2(g) + 2NO_2(g) + 5H_2O(g) + 3Cl_2(g) \quad (7)$$

$$PtS \cdot 2NH_3(s) + PtS(s) + PtS_2(s) + O_2(g) \overset{365°C}{\rightarrow} 3PtS(s) + SO_2(g) + 2NH_3(g) \quad (8)$$

$$PtS(s) + O_2(g) \overset{385°C}{\rightarrow} Pt(s) + SO_2(g) \quad (9)$$

The intermediates as well as the final product of the decompositions have been isolated and analysed by vibrational spectroscopy, X-ray diffractometry and chemical analysis.

The values of the non-isothermal kinetic parameters of reactions (6) and (7) are listed in Tables 4 and 5. A satisfactory agreement among the values

TABLE 4

Values of the non-isothermal kinetic parameters of reaction (6) at $\beta = 2.63$ K min^{-1}

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	0	6.93×10^3	0.38
Flynn–Wall	0	8.38×10^4	9.00
Modified Coats–Redfern	0	8.02×10^3	0.20

TABLE 5

Values of the non-isothermal kinetic parameters of reaction (7) at $\beta = 2.63$ K min^{-1}

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats—Redfern	1.1	3.78×10^4	3.81×10^{11}
Flynn–Wall	1.1	3.81×10^4	5.20×10^{11}
Modified Coats–Redfern	1.0	3.80×10^4	4.54×10^{11}

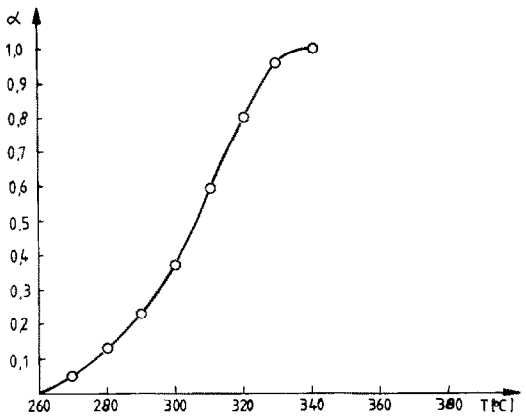

Fig. 1. TG curve regenerated in coordinates α and T (°C) for reaction (2) at $\beta = 2.8$ K min^{-1}: ———, calculated curve; o, experimental points.

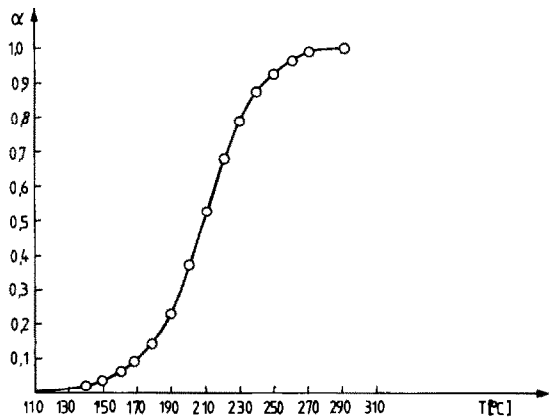

Fig. 2. TG curve regenerated in coordinates α and T (°C) for reaction (7) at $\beta = 2.63$ K min^{-1}: ———, calculated curve; o, experimental points.

of the non-isothermal kinetic parameters can also be observed for these cases.

As shown in Table 5, the values of the pre-exponential coefficient for $n = 1$ are close to those predicted by the theory of transition state [8].

The TG curves regenerated in coordinates α and T (°C) using the Coats–Redfern kinetic parameter values are given in Figs. 1 and 2. As can be seen, the experimental points lie practically on these curves.

CONCLUSIONS

The thermal decomposition steps for $[PdC_{19}H_{18}N_2S_2]Cl_2 \cdot H_2O$ and $[Pt_3C_{38}H_{36}N_4S_4]Cl_6 \cdot 3H_2O$ were derived. Where possible, the values of the non-isothermal kinetic parameters have been determined for the individual

decomposition steps. A satisfactory agreement was obtained among the values of the non-isothermal kinetic parameters obtained by the three methods applied.

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