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THERMAL ANALYSES OF COORDINATION COMPOUNDS
II. Thermal decomposition of palladium complexes with triphenylphosphine, triphenylarsine and triphenylstibine

R. S. Barbiéri, C. R. Belatto[1] and A. C. Massabni[1]*

Departamento de Química, Universidade Federal de Viçosa, 36570-000, Viçosa, MG, Brazil
[1]Instituto de Química, Universidade Estadual Paulista "Julio de Mesquita Filho", 14800-900, Araraquara, SP, Brazil

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Abstract

The compounds [$PdCl_2L_2$] and [PdL_4] (L = PPh_3, $AsPh_3$, $SbPh_3$) were studied by thermogravimetric and differential thermal analyses in air. The residues of thermal decomposition consist of metallic palladium, except in the case of the complexes containing $SbPh_3$, when the residues are palladium and antimony mixtures in appropriate proportions with respect to the stoichiometry of the related complexes.

Keywords: palladium complexes, thermal analysis

Introduction

The complexes of bivalent and zerovalent palladium [$PdCl_2L_2$] and [PdL_4] [L = PPh_3 (triphenylphosphine), $AsPh_3$ (triphenylarsine) or $SbPh_3$ (triphenylstibine), apart from being precursors for the synthesis of organometallic compounds [1–3] are used in homogeneous catalysis [4–6]. Not withstanding the importance of these compounds, they have merited little attention with respect to thermal analysis, except for the application of high-temperature microcalorimetry for thermal decomposition studies on selected complexes with phosphines [7]. The present investigation reports the use of thermogravimetric analysis (TG) and differential thermal analysis (DTA) in air for study of the above-mentioned complexes.

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* Author to whom correspondence should be addressed.

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Experimental

The DTA curves in the range 25–900°C were obtained with the DTA RB-12 equipment manufactured by BP Engenharia, Industria e Comércio Ltda, with two ovens and connected to an ECB X-T RB-102 recorder. The control was α-alumina previously calcined at 1100°C, which was also used to dilute samples up to 25% in mass. The rate of heating was 10.0 $\mathrm{deg \cdot min^{-1}}$, with a recording speed of 15.0 $\mathrm{cm \cdot h^{-1}}$.

TG curves, also in the range 25–900°C, were plotted with the TGS-2 equipment from Perkin-Elmer. 4–8 mg samples were used, with a heating rate of 10.0 $\mathrm{deg \cdot min^{-1}}$ and a recording speed of 30.0 $\mathrm{cm \cdot h^{-1}}$.

The infrared (IR) spectra of the complexes in the region 4000–200 $\mathrm{cm^{-1}}$ were obtained with a Perkin-Elmer 567 spectrophotometer, using CsI pellets.

The elementary analyses of carbon and hydrogen were carried out a CETEC (Fundãçao Centro Tecnológico de Minas Gerais – Technological Center Foundation of Minas Gerais) in Belo Horizonte – MG, Brazil, and at the Institute de Química da USP (USP Institute of Chemistry) in São Paulo - SP, Brazil.

The complexes $[PdCl_2L_2]$ and $[PdL_4]$ were prepared from $Na_2[PdCl_4]$ by methods described in the literature [8–11], and characterized through their IR spectra and by elementary analyses of carbon and hydrogen.

Results and discussion

Figures 1 and 2 depict DTA and TG curves for the investigated complexes and free ligands, respectively. Table 1 lists the temperatures observed in the DTA curves relating to the mass losses observed in the TG curves.

Table 1 Temperatures of DTA peaks of the complexes and ligands

Complexes and ligands	Peak temperatures / °C	
	Exothermic	Endothermic
$[PdCl_2(PPh_3)_2]$	230–315–375–535	–
$[PdCl_2(AsPh_3)_2]$	227–347–413–487	250
$[PdCl_2(SbPh_3)_2]$	150–453–753	227
$[Pd(PPh_3)_4]$	100–120–253–373–423	–
$[Pd(AsPh_3)_4]$	210–290–370–453–510	173
$[Pd(SbPh_3)_4]$	173–450–793	220
PPh_3	290–500–560	80–395
$AsPh_3$	360–480–570–590	60
$SbPh_3$	170–280–350–510–530–755–780	55

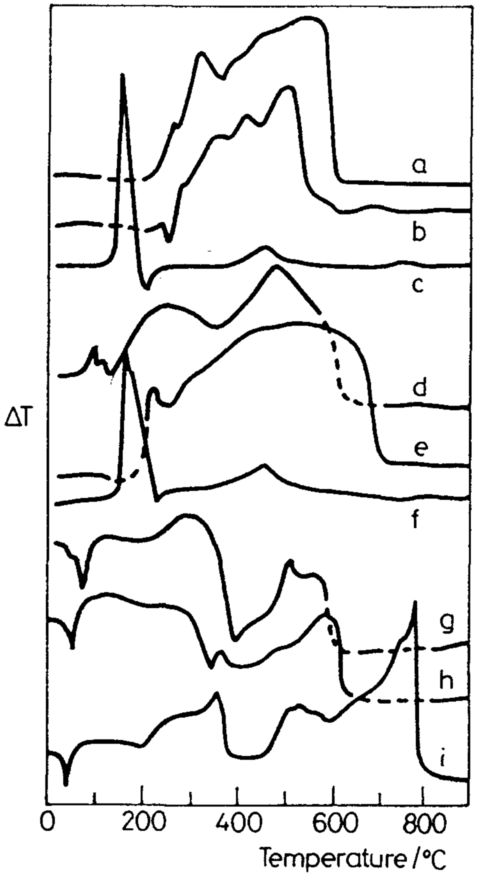

Fig. 1 DTA curves of the palladium compounds, diluted to 25% in alumina. Heating rate: 10.0 deg·min^{-1} ; (a) [$PdCl_2(PPh_3)_2$], (b) [$PdCl_2(AsPh_3)_2$], (c) [$PdCl_2(SbPh_3)_2$], (d) [$Pd(PPh_3)_4$], (e) [$Pd(AsPh_3)_4$] (f) [$Pd(SbPh_3)_4$], (g) PPh_3, (h) $AsPh_3$, (i) $SbPh_3$

The relative thermal stabilities of the complexes may be established by comparison of the initial decomposition temperatures displayed in Table 2. The bivalent complexes [$PdCl_2L_2$] are more stable than the zerovalent complexes [PdL_4]. The series of relative thermal stability are as follows:

$$[PdCl_2(PPh_3)_2] > [PdCl_2(AsPh_3)_2] > [PdCl_2(SbPh_3)_2]$$

$$[Pd(AsPh_3)_4] > [Pd(SbPh_3)_4] > [Pd(PPh_3)_4]$$

The disorder observed with respect to [$Pd(PPh_3)_4$] may be attributed to the fact that this compound, even in the solid state, is chemically unstable in air, undergoing decomposition in a few hours. The process involved in its thermal decomposition is probably not simple but involves formation of the carbonato complex and oxidation of the ligand to the phosphine oxide. This may be deduced from IR spectra traced during 2–3 h on a sample of [Pd(PPh$_3$)$_4$] kept in air. Gradually, a strong and broad band is observed at 1680 cm^{-1} which is attributed to the stretching of coordinated carbonyl [12–14], and another strong band, centred at 1190 cm^{-1}, is formed [15], which can be attributed to the P–O stretching of triphenylphosphine oxide. The process of decomposition of [Pd(PPh$_3$)$_4$] in air is accelerated at temperatures higher than environmental, as demonstrated by the TG and DTA curves for the compound. At approximately 70°C, the complex [Pd(PPh$_3$)$_4$] undergos a slight increase in mass (curve d, Fig. 2) in an exothermic process that proceeds in two steps, corresponding to the peaks at 100 and 120°C in the corresponding DTA curve (curve d, Fig. 1).

Analysis of the TG curves of the complexes suggests that, for the two series of compounds investigated, the rate of thermal decomposition increases in the sequence PPh$_3$ < AsPh$_3$ < SbPh$_3$, the slopes of the curves increasing in that sequence. An inverse tendency is observed for the final temperature of the processes of thermal decomposition, as indicated in Table 2.

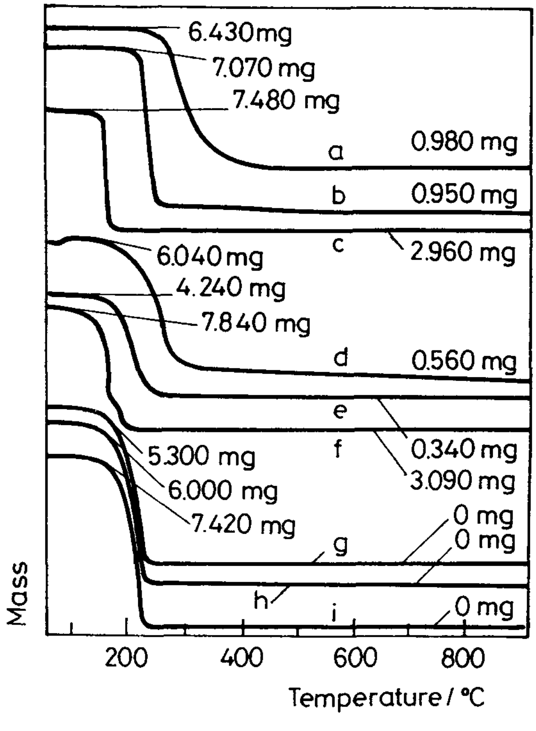

Fig. 2 TG curves of the palladium compounds. Heating rate: 10.0 deg·min^{-1}
(a) [PdCl$_2$(PPh$_3$)$_2$], (b) [PdCl$_2$(AsPh$_3$)$_2$], (c) [PdCl$_2$(SbPh$_3$)$_2$], (d) [Pd(PPh$_3$)$_4$], (e) [Pd(AsPh$_3$)$_4$], (f) [Pd(SbPh$_3$)$_4$], (g) PPh$_3$, (h) AsPh$_3$, (i) SbPh$_3$

Table 2 Initial and final temperatures of the thermodecomposition processes of the complexes

Complexes	Temperature / °C	
	Initial	Final
$[PdCl_2(PPh_3)_2$	250	550
$[PdCl_2(AsPh_3)_2]$	200	500
$[PdCl_2(SbPh_3)_2]$	140	190
$[Pd(PPh_3)_4]$	50	700
$[Pd(AsPh_3)_4]$	140	400
$[Pd(SbPh_3)_4]$	160	300

As concerns the mechanisms of thermal decomposition of the complexes $[PdCl_2(PPh_3)_2]$, $[PdCl_2(AsPh_3)_2]$, $[Pd(PPh_3)_4]$ and $[Pd(AsPh_3)_4]$, the TG curves (curves a, b, d and e, respectively, Fig. 2) indicate that they are similar, regardless of the presence of coordinated chlorine. The thermal decomposition occurs in one step, the metal being formed. During the process of thermal decomposition, evolution of free ligand is observed. This may be verified by slowly heating each of the complexes in a test-tube. A white material sublimes onto the upper portion of the tube. Determination of the melting point identifies this as triphenylphosphine or triphenylarsine, as the case may be.

With respect to $[PdCl_2(SbPh_3)_2]$ and $[Pd(SbPh_3)_4]$, the thermal decomposition appears to occur in two consecutive steps, the second step being more defined for the zerovalent complex. For both compounds, the final product consists of palladium and antimony. Dissolution of the final product of each complex in hot concentrated nitric and hydrochloric acids (*aqua regia*), evaporation of the solution and its separation into two aliquots was followed by qualitative tests for the identification of antimony. Through one of the aliquots, hydrogen sulphide gas was passed, resulting in an orange-red precipitate of antimony pentasulphide. To the other aliquot, a large volume of water was added, resulting in the formation of a white precipitate of basic salts of antimony with diverse compositions [16].

Table 3 contains data relating to the initial masses of the palladium complexes subjected to TG and the final masses of the residues obtained after decomposition. For the compounds with PPh_3 and $AsPh_3$, the quantities of the residues are in agreement with the palladium content expected for these complexes. In the cases of $[PdCl_2(SbPh_3)_2]$ and $[Pd(SbPh_3)_4]$, the quantities of the residues correspond to the stoichiometric composition Pd+2Sb and Pd+4Sb, respectively.

Table 2 reveals, that the final temperatures of thermal decomposition for the complexes $[PdCl_2(SbPh_3)_2]$ and $[Pd(SbPh_3)_4]$ are 190 and 300°C, respectively. Each of these compounds, however, presents two exothermic peaks in the DTA curves, at 453 and 753°C for the former, and at 450 and 793°C for the latter. These peaks may be attributed to phase transitions and variations of the composition of the metallic alloys formed by palladium and antimony [17], which comprise the residues of thermal decomposition of the compounds.

Table 3 Thermogravimetric data for the complexes and ligands studied

Complexes and ligands	Initial mass /mg	Final mass /mg (% residue)	Theoretical/ % (residue)	Pd /% (theoretical %)
$[PdCl_2(PPh_3)_2]$	6.430	0.980(15.24)	15.16(Pd)	15.24(15.16)
$[PdCl_2(AsPh_3)_2]$	7.070	0.950(13.44)	13.47(Pd)	13.44(13.47)
$[PdCl_2(SbPh_3)_2]$	7.480	2.960(39.57)	39.61(Pd+2Sb)	12.03(12.04)
$[Pd(PPh_3)_4]$	6.040	0.560(9.27)	9.21(Pd)	9.27(9.21)
$[Pd(AsPh_3)_4]$	4.240	0.340(8.02)	7.99(Pd)	8.02(7.99)
$[Pd(SbPh_3)_4]$	7.840	3.090(39.41)	39.07(Pd+4Sb)	7.01(7.01)
PPh_3	5.300	0		
$AsPh_3$	6.000	0		
$SbPh_3$	7.420	0		

Figures 1 and 2, g, h and i present DTA and TG curves of the free ligands PPh_3, $AsPh_3$ and $SbPh_3$, respectively. The DTA curves contain endothermic peaks at 80, 60 and 55°C, corresponding to the respective melting points. Literature data give melting ranges of 79–81°C for PPh_3, 60–62°C for $AsPh_3$ and 52–54°C for $SbPh_3$ [18]. The TG curves indicate a total loss of mass, no residue being observed. On gentle heating of the free ligands in a test-tube, it was possible to detect the sublimation of these ligands, without apparent decomposition.

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References

1 F. R. Hartley, Organometal. Chem. Rev. A, 6 (1970) 119.
2 P. A. Chaloner, J. Organometal. Chem., 337 (1987) 431.
3 P. A. Chaloner, Coord. Chem. Rev., 72 (1986) 1.
4 R. Tamura, Y. Kay, M. Karihana, K. Hayashi, M. Tsuji, T. Nakamura and D. Oda, J. Org. Chem., 51 (1986) 4375.
5 Y. Ichinosc, H. Oda, K. Oshim and K. Utimoto, Bull. Chem. Soc. Jpn., 60 (1987) 3460.
6 R. S. Barbiéri, A. C. Massabni and C. R. Belatto, Seminário Brasileiro de Catálise, 5. Guarujá-SP, 1989. Anais, Rio de Janeiro, IBP, 1989, p. 240.
7 G. A. Takhin, H. A. Skinner and A. A. Zaki, J. Chem. Soc., Dalton Trans, (1984) 371.

8 L. Malatesta and M. Angoletta, J. Chem. Soc., (1957) 1186.
9 D. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian and D. A. White, J. Chem. Soc., (1969) 1793.
10 R. S. Barbiéri, S. I. Klein and A. C. Massabni, J. Chem. Soc., Chem. Commun., (1987) 1617.
11 R. S. Barbiéri, C. R. Belatto and A. C. Massabni, Quím. Nova, 14 (1991) 212.
12 H. C. Clark, A. B. Goel and C. S. Wong, Inorg. Chim. Acta, 34 (1979) 159.
13 P. J. Hayward, D. M. Blake, C. J. Nyman and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1969) 987.
14 C. J. Nyman, E. Wimore and G. Wilkinson, J. Chem. Soc., (1968) 561.
15 K. A. Jensen and P. H. Nielsen, Acta Chem. Scand., 17 (1875) 1973.
16 A. I. Vogel, Química Analítica Qualitativa, 5a ed., Ed. Mestre Jou, São Paulo 1981, p. 260.
17 J. W. Mellor, Inorganic and Theoretical Chemistry, vol. IX, Longmans, London 1957, p. 416.
18 Dictionary of Organic Chemistry, 4nd ed., Eyre & Comercial Stodiswoode, London 1965.

Zusammenfassung — Mittels TG und DTA in Luft wurden die Verbindungen $[PdCl_2L_2]$ und $[PdL_4]$ (L = PPh_3, $AsPh_3$, $SbPh_3$) untersucht. Die Rückstände der thermischen Zersetzung bestehen aus metallischem Palladium, mit Ausnahme des Falles der Komplexe mit $SbPh_3$, wo die Rückstände Gemische aus Palladium und Antimon in einer der Stöchiometrie der fraglichen Komplexe entsprechenden Menge sind.