Thermochimica Acta, 235 (1994) 285–289
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01548-H

Note

Thermal analysis of coordination compounds. Part 1. Thermodecomposition of nickel(II) triphenylphosphine complexes with halides, nitrate, and thiocyanate

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(Received 14 June 1993; accepted 17 August 1993)

Abstract

The compounds $[NiX_2(PPh_3)_2]$ (where X is Cl^-, Br^-, I^-, NO_3^-, NCS^-; and PPh_3 is triphenylphosphine) were prepared and characterized by infrared and atomic absorption spectroscopies and by carbon and hydrogen analyses. Simultaneous thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of these complexes were recorded in air. The decrease in mass observed indicates conversion of the complexes to oxides. The thermal decomposition of the halogen and nitrate complexes occurred in a number of steps; the thiocyanate complex decomposed in a single step.

INTRODUCTION

The compounds $[NiX_2(PPh_3)_2]$, where X is Cl^-, Br^-, I^-, were described by Reppe and Sweckendiek [1] and Yamamoto [2], and those where X is NO_3^-, NCS^-, were described by Venanzi [3].

Solid state magnetic susceptibility measurements and X-ray diffractometry results reported by Venanzi [3] and Garton et al. [4] showed that the complexes are paramagnetic and have pseudo-tetrahedral structures, except the thiocyanate complex which is diamagnetic and has a trans-planar configuration [3, 5]. Nuclear magnetic resonance [6] and infrared and Raman vibrational studies [7] were also used in the structural determinations.

Complexes with triphenylphospine as ligand have been studied extensively in coordination chemistry, mainly because of their applications in

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homogeneous catalysis. Nickel(II) triphenylphosphine complexes are used, for example, in catalytic processes involving Grignard compounds [8, 9], alkene oligomerization [10], and ketone preparations [11].

The thermal properties of these compounds have not been investigated extensively. The present work deals with the thermal decomposition of nickel(II) triphenylphosphine complexes with halides, nitrate, and thiocyanate.

EXPERIMENTAL

The thermodecomposition of the complexes between 50 and 850°C was carried out on a TG-50 balance coupled to a TC-10-A processor of a Mettler TA-3000 system. Samples of less than 10 mg were used and the heating rate was $20°C\,min^{-1}$. The studies were carried out in static air atmosphere at ambient pressure.

The infrared spectra were obtained on a Perkin-Elmer 425 spectrophotometer using potassium bromide pastille techniques.

The microanalyses were carried out by the Instituto de Química, USP, in São Paulo-SP, Brazil.

Two methods were used to determine the nickel content: precipitation with dimethylglyoxime [12] and atomic absorption spectrophotometry, using an Intralab AA-1475 spectrophotometer.

The uncorrected melting points were determined on an FP-2 Mettler system.

The complexes were synthesized by methods described by Venanzi [3] and Cotton et al. [13]. All chemicals were used without further purification.

RESULTS AND DISCUSSION

Table 1 presents the results of the carbon, hydrogen, and nickel elemental analyses of the compounds prepared, of formulae $[NiX_2(PPh_3)_2]$, where X is Cl^-, Br^-, I^-, NO_3^-, NCS^-. These data agree with information obtained from the infrared spectra of the complexes and confirm the proposed formulae. The characteristic colors and melting points of the complexes are in agreement with the literature data [2, 3] and are also presented in Table 1.

Figure 1 shows the simultaneous thermogravimetric (TG) and the derivative thermogravimetric curves for $[NiCl_2(PPh_3)_2]$ (**I**), $[NiBr_2(PPh_3)_2]$ (**II**), $[NiI_2(PPh_3)_2]$ (**III**), $[Ni(NO_3)_2(PPh_3)_2]$ (**IV**), and $[Ni(NCS)_2(PPh_3)_2]$ (**V**). Table 2 gives the initial and final temperatures of the thermodecomposition processes.

From the analysis of the TG and DTG curves, it was possible to establish the following relative thermal stability series: **V** > **IV** > **I** > **II** > **III**. This series was obtained by comparison of the initial temperatures of thermodecomposition of the complexes presented in Table 2.

TABLE 1

Analytical data, color and melting points for the nickel(II) triphenylphosphine complexes

Complexes	% C found (calc.)	% H found (calc.)	% Ni found (calc.)	Color	m.p./°C
$[NiCl_2(PPh_3)_2]$	66.16 (66.10)	4.71 (4.62)	9.01 (8.97)	Blue	246–248
$[NiBr_2(PPh_3)_2]$	58.26 (58.18)	4.95 (4.88)	7.93 (7.90)	Dark green	222–224
$[NiI_2(PPh_3)_2]$	51.75 (51.65)	3.66 (3.61)	7.08 (7.01)	Brown	219–221
$[Ni(NO_3)_2(PPh_3)_2]$	61.32 (61.13)	4.16 (4.28)	8.30 (8.29)	Green	221–222
$[Ni(NCS)_2(PPh_3)_2]$	61.73 (61.82)	4.43 (4.32)	8.37 (8.39)	Red	216–217

When the spectrochemical series of the ligand involved is considered [14], i.e. $NO_3^- > Cl^- > SCN^- > Br^- > I^-$, good agreement is observed with the relative thermal stability sequence proposed for the nickel(II) complexes under study, except for compound **V**. This discrepancy, however, is explained by geometric factors. The nickel(II) thiocyanate complex has a planar structure, while the other complexes are tetrahedral [3].

The thermodecomposition mechanisms are distinct for each compound. However, there is a common, major peak at 400–450°C in the DTG curves, which may involve liberation of free triphenylphosphine. In fact, when each compound is heated in a test tube, white material is formed at the top of the tube. From melting point determinations and infrared spectroscopy, this material was identified as triphenylphosphine.

For the compounds **I**, **II**, and **III**, the thermodecomposition mechanism involved is very complex. This main step is preceded by partial oxidation of the triphenylphosphine to triphenylphosphine oxide. This is characterized by a mass increase at 230, 200, and 190°C, respectively, in the TG and DTG curves. On heating these complexes at 240°C for 15 min, the respective infrared spectra show a new strong band at 1200 cm^{-1} which can be attributed to the P–O stretching vibration of triphenylphosphine oxide [15]. A similar behavior was also observed by Barbiéri [16] for zero-valent palladium complexes with triphenylphosphine.

The thermodecomposition of compound **IV** probably proceeds with liberation of NO_2 in two consecutive steps, corresponding to the 290 and 305°C peaks on the DTG curve, followed by triphenylphosphine liberation at 400°C. The TG and DTG curves for complex **V** suggest only a one-step thermodecomposition mechanism. For compounds **IV** and **V**, no mass

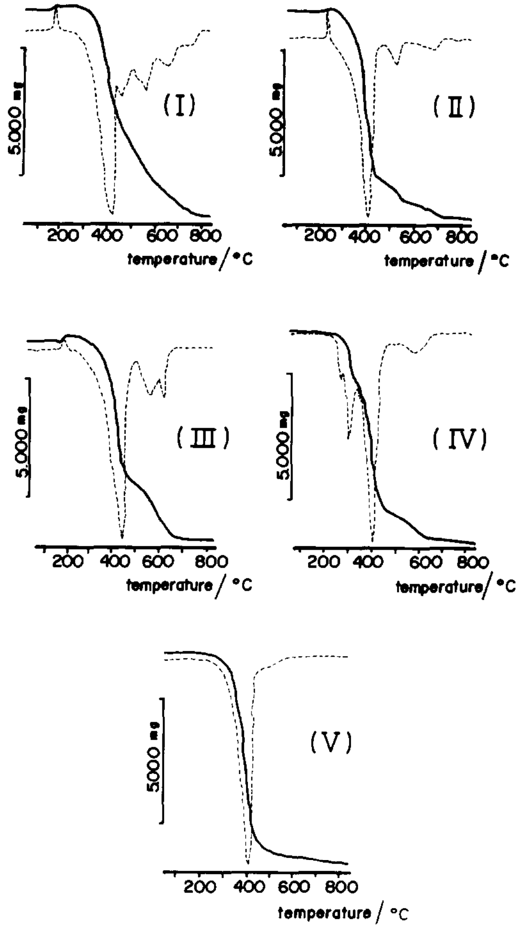

Fig. 1. TG (——) and DTG (– – – –) curves of **I**, [$NiCl_2(PPh_3)_2$]; **II**, [$NiBr_2(PPh_3)_2$]; **III**, [$NiI_2(PPh_3)_2$]; **IV**, [$Ni(NO_3)_2(PPh_3)_2$]; and **V**, [$Ni(NCS)_2(PPh_3)_2$].

TABLE 2

Initial and final temperatures (°C) of the thermodecomposition processes and NiO contents of the nickel(II) triphenylphosphine complexes

Complexes	Temperatures/°C		Mass/mg		NiO/%	
	Initial	Final	Initial	Final	Found	Calc.
[$NiCl_2(PPh_3)_2$]	230	720	9.197	1.053	11.45	11.42
[$NiBr_2(PPh_3)_2$]	200	660	9.977	0.998	10.26	10.05
[$NiI_2(PPh_3)_2$]	190	800	9.723	0.871	8.96	8.92
[$Ni(NO_3)_2(PPh_3)_2$]	240	760	9.228	0.973	10.54	10.56
[$Ni(NCS)_2(PPh_3)_2$]	250	800	9.070	0.965	10.64	10.68

increase was observed during the heating, and, consequently, triphenylphosphine oxide was not formed. In fact, the infrared spectra of these compounds obtained after heating at 240°C did not show the characteristic P–O stretching for the triphenylphosphine oxide.

Nickel oxide was obtained as a residue from the decomposition of all the complexes. The mass obtained established the NiO contents of the studied complexes. The results are presented in Table 2 and are in good agreement with the theoretical values.

ACKNOWLEDGMENT

The authors acknowledge research support from the Brazilian Government (CNPq).

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