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THERMAL DECOMPOSITION OF PHOSPHINE COMPLEXES OF NICKEL (II) DIHALIDES

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ABSTRACT

Thermogravimetric measurements show that complexes of nickel (II) dihalides with alkyl and aryl substituted phosphines in an oxygen containing atmosphere start to decompose near or above 200 °C yielding solid phases based on nickel oxide and phosphorus pentoxide.

INTRODUCTION

Complexes of nickel (II) compounds, particularly those with nitrogen coordinated ligands, and their thermal dissociation reactions have been studied in great detail[1]. These dissociation reactions generally proceed in a straightforward manner. Most of the complexes with nitrogen coordinated ligands degrade step-wise giving compounds with a lower ligand metal ion content. This paper presents a study of the thermal stability in an oxygen containing atmosphere of nickel (II) dihalide phosphine complexes, $NiX_2(PR_3)_2$, where X = halogen and R = alkyl or aryl, by thermogravimetric analysis (TGA). In connection with these studies it was of interest to search for parallels in the thermal behavior of complexes having phosphorus bonded ligands and those having nitrogen bonded ligands. A related study of the thermal properties of cobalt (II) dihalide complexes of phosphines has been published elsewhere.

EXPERIMENTAL

Materials

Triphenylphosphine was obtained from Eastman and tri-n-butylphosphine from M&T·Chemicals. Di-n-butylphenylphosphine was prepared from dichlorophenylphosphine and n-butyl lithium in 73% yield, b.p. 90 °C at 1 mm and n-butyldiphenylphosphine was synthesized similarly from chlorodiphenylphosphine and n-butyl lithium in 73% yield, b.p. 120 °C at 0.2 mm. The nickel (II) dihalides were purchased from Fischer Scientific or Alfa Inorganics.

Preparation of Complexes

The complexes used in this study were prepared by combining solutions of the nickel (II) dihalides with solutions of the phosphine in the mole proportions 1:2

following procedures reported in the literature[3-6]. Several of these complexes have been also prepared and characterized by several other investigators[7,8] (Table I).

TABLE I

NICKEL (II) DIHALIDE PHOSPHINE COMPLEXES INVESTIGATED IN THIS STUDY

Complex	*M.p. (lit.) (°C)*	*Yield (%)*	*Reference*
$NiCl_2(PPh_3)_2$	240, dec. (247–250)[a]	79	3
$NiBr_2(PPh_3)_2$	220–222 (222–225)[b]	44	3
$NiI_2(PPh_3)_2$	215–220 (218–220)[c]	70	3
$NiCl_2(PBuPh_2)_2$	147–152 (149–150)[d]	85	4
$NiCl_2(PBu_2Ph)_2$	58–59 (56–57)	74	4
$NiCl_2(PBu_3)_2$	50–55 (56–57)	75	5

[a] Lit.[6]: m.p. 221–222°C.
[b] Lit.[6]: m.p. 205–206°C; Lit.[7]: m.p. 223°C.
[c] Lit.[6]: m. p. 225°C.
[d] Lit.[8]: m.p. 143–147°C.

Apparatus

The instrument used for the thermogravimetric measurements was an Aminco Thermo-Grav manufactured by the American Instrument Co., Silver Springs, Md. The sample size generally amounted to about 200 mg and the sweep gas in all cases was a mixture of 10% oxygen and 90% helium at a flow rate of 50 cm^3/min. The heating rate was 3°C/min.

RESULTS AND CONCLUSIONS

Triphenylphosphine Complexes

The complexes of the general formula $NiX_2(PPh_3)_2$ are paramagnetic with magnetic moments corresponding to two unpaired electrons. An X-ray study of $NiCl_2(PPh_3)_2$ indicates a tetrahedral configuration for this compound[9].

In an earlier study of some of the thermal properties of bis(triphenylphosphine) complexes of nickel (II) dihalides it was observed[10] that upon heating $NiBr_2(PPh_3)_2$ in air a sublimate was obtained which consisted of triphenylphosphine oxide. However, in nitrogen atmosphere the sublimate was triphenylphosphine. Weight loss studies at constant temperature (250°C) in nitrogen showed that the amount of triphenylphosphine dissociated under these conditions was 88% of the theoretical for $NiCl_2(PPh_3)_2$, 80% for $NiBr_2(PPh_3)_2$ and 29% for $NiI_2(PPh_3)_2$, indicating an increase of stability in that order.

The present paper describes weight loss *vs.* temperature studies of nickel (II) dihalide bis(triphenylphosphine) complexes. As shown in Fig. 1, using the minimum TGA dissociation temperatures as the criteria for determining thermal stability, the order of increasing stability is chloride < bromide < iodide. This order is in agreement with the previously reported data[10] and with the order established for ammine and other nitrogen bonded ligands in nickel (II) dihalide complexes[1]. For comparison purposes the TGA curve for the ligand triphenylphosphine itself is shown in Fig. 1 also. It is seen that the ligand, when heated in the thermo-balance under comparable conditions, starts to distill out of the sample holder at about 150°C with this process having gone to completion at < 275°C whereas the decomposition temperature of the complexes is > 180°C. This indicates that the rate-determining step in the thermal decomposition of the complex is the dissociation of the triphenylphosphine ligand rather than the volatilization of the ligand after it has been released from coordination with the metal ion. Upon further temperature increase beyond the occurrance of the initial weight loss, simultaneous distillation of the volatile triphenylphosphine and oxidation of part of the triphenylphosphine takes place. This oxidation apparently is catalyzed by nickel ions since in their absence the phosphine distills cleanly and quantitatively out of the sample holder. Also, cobalt ions were found[2] to catalyze the oxidation of triphenylphosphine by oxygen. It is visualized that the oxidation process proceeds *via* triphenylphosphine oxide, diphenylphosphinic acid, phenylphosphinic acid to phosphate. Breaks in some of the TGA curves seen above about 300°C may be indicative of such a mechanism. However, in no instances stable intermediates such as complexes with only one phosphine ligand were realized during the thermal decomposition.

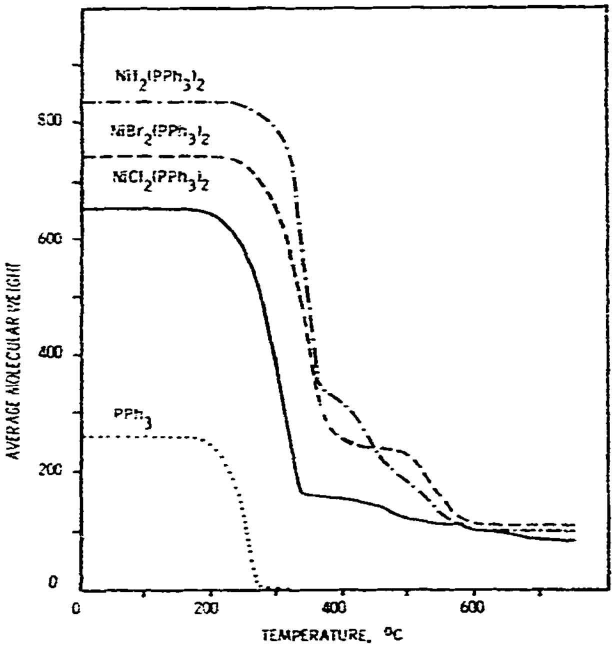

Fig. 1. TGA curves of $NiX_2(PPh_3)_2$ and PPh_3.

The average apparent molecular weight of the residues obtained after the mass loss curves have become horizontal ranges from 101 for the iodo complex, to 108 for the bromo complex, and 110 for the chloro complex. Elemental analysis of the residue of the thermal decomposition of $NiCl_2(PPh_3)_2$ gave 40.5% nickel and 12.9% phosphorus and small amounts of chlorine. This is interpreted to mean that solid phases consisting of nickel oxide and phosphorus pentaoxide were formed. Similar solid materials based on Co_3O_4 and P_2O_5 were obtained as a result of the thermal decomposition of analog cobalt complexes, $CoX_2(PPh_3)_2$.

Other phosphine complexes

The additional phosphine complexes investigated in this study were of the general formula $NiCl_2[P(n\text{-}C_4H_9)_n(C_6H_5)_{3-n}]_2$, where $n = 1, 2$, or 3. The n-butyldiphenyl complex ($n = 1$) at low temperatures may be obtained as the square planar structure being of dark red color. This form, however, is unstable at room temperature and rapidly isomerizes within a few minutes to the blue-purple tetrahedral form[8]. The latter form was the one used in the present work. The complexes for $n = 2$ and 3 are diamagnetic dark red crystals and thus were assigned a transplanar structure[4].

The weight loss curves in Fig. 2 show that the complexes for $n = 1, 2$, and 3 do not differ greatly in their thermal stability. Thermal decomposition is seen to occur in the range from 175 to 200°C which is higher than the temperature at which triphenylphosphine itself is volatilized under comparable conditions. Since the phosphines $P(n\text{-}C_4H_9)_n(C_6H_5)_{3-n}$ are more volatile than triphenylphosphine, the temperature at which weight loss is first observed for these complexes clearly is determined by the stability of the complexes and not by the rate of volatilization of the ligands. It appears further that there is no significant difference in the stabilities of these complexes when they are compared with the triphenylphosphine complex of $NiCl_2$, the thermal stability of which is depicted in Fig. 1.

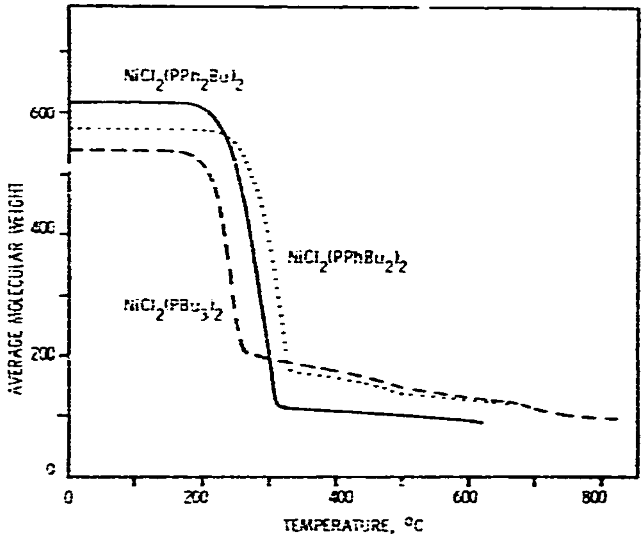

Fig. 2. TGA curves of nickel (II) dichloride phosphine complexes $NiCl_2(PBu_nPh_{3-n})_2$.

The average apparent molecular weight of the residues of the thermal degradation of the above complexes in the oxygen containing atmosphere at 650°C ranges from 97 for the tri-n-butylphosphine complex to 125 and 127 for the n-butyldiphenyl and di-n-butylphenyl phosphine complex, respectively. The conclusions with regard to the formation and the nature of the residue of the thermal decomposition of these complexes are the same as were developed for the triphenylphosphine complexes described above.

REFERENCES

1 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967.
2 K. Moedritzer and R. E. Miller, *J. Thermal Analysis*, in the press.
3 L. M. Venanzi, *J. Chem. Soc.*, (1958) 719.
4 C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, (1961) 2705.
5 K. A. Jensen, *Z. Anorg. Allgem. Chem.*, 229 (1936) 265.
6 K. Yamamoto, *Bull. Chem. Soc. Japan.*, 27 (1954) 501.
7 W. Reppe and W. J. Schweckendieck, *Ann.*, 560 (1948) 104.
8 R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 4 (1965) 1701.
9 G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6 (1964) 1.
10 K. Yamamoto and M. Oku, *Bull. Chem. Soc. Japan.*, 27 (1954) 509.