

THERMAL STABILITY OF PHOSPHINE AND PHOSPHINE OXIDE COMPLEXES OF COBALT(II) DIHALIDES

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Thermogravimetric measurements show that complexes of cobalt(II) dihalides with aryl and alkyl substituted phosphines and triphenylphosphine oxide in an oxygen containing atmosphere decompose to yield solid phases consisting of Co_3O_4 and P_2O_5 .

The thermal properties of cobalt(II) dihalide complexes with coordinatively bonded nitrogen ligands have been studied in great detail [1]. In many of these cases complexes upon heating dissociate one or more of the coordinated ligands resulting in new species which generally remain stable within limited temperature ranges. These new species, in turn, upon further heating lost the remaining coordinatively bonded ligands in a series of additional distinct stoichiometric steps. In the course of such studies certain generalizations with regard to the thermal dissociation of cobalt(II) halide complexes were established. In view of this work on the nitrogen coordinated complexes it was therefore of interest to investigate the thermal properties of phosphine and phosphine oxide complexes of cobalt(II) dihalides and to explore the formation of intermediate dissociation products. Attempts will be made to deduce general conclusions with respect to the thermal stabilities of these compounds.

Experimental

Materials. Triphenylphosphine and triphenylphosphine oxide were obtained from Eastman, bis(1,2-diphenylphosphino)ethane from Strem Chemical Company. Tri-*n*-butylphosphine was purchased from M & T Chemicals. The *n*-butyl-diphenylphosphine was prepared from chlorodiphenylphosphine (Aldrich) and *n*-butyl lithium in 73% yield, b.p. 120° at 0.2 mm pressure, di-*n*-butylphenylphosphine was made analogously from dichlorophenylphosphine (Fischer Scientific) and *n*-butyl lithium in 73% yield, b.p. 90° at 1 mm pressure. Anhydrous cobalt(II) dihalides were purchased from Alfa Inorganics and the corresponding hydrates from Fischer Scientific.

Preparation of complexes. The phosphine [2-6] and phosphine oxide [7, 8] complexes were prepared according to methods of the literature by combining

one mole of cobalt(II) dihalide with two moles of the respective phosphorus compound in a suitable solvent. After recrystallization the samples were dried in vacuo for 48 hours. The complexes prepared in this study are summarized in Table 1. Two of these are believed to be new and their syntheses therefore are described below in detail.

Table 1

Cobalt(II) halide phosphine and phosphine oxide complexes investigated in this study

	M.p., °C (lit.)	Yield, %	Reference
CoCl ₂ (PPh ₃) ₂	246 (247—251)	63	3, 4
CoBr ₂ (PPh ₃) ₂	218—210 (218—219)	89	3, 4
CoI ₂ (PPh ₃) ₂	210—214 (209—214)	86	3, 4
CoCl ₂ (PPh ₂ Bu) ₂	162	97	
CoCl ₂ (PPhBu ₂) ₂	79	79	
CoCl ₂ (PBu ₃) ₂	—*	100	2
CoCl ₂ (Ph ₂ PCH ₂ CH ₂ PPh ₂)	350—354	65	6
CoCl ₂ (Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂	115 dec. (120—125 dec.)	46	5, 6
CoCl ₂ (OPPh ₃) ₂	242 (233)	71	7
CoBr ₂ (OPPh ₃) ₂	228 (223)	68	8
CoI ₂ (OPPh ₃) ₂	235 (232)	58	8

* Blue oil at room temperature.

Dichlorodi(n-butyl-diphenylphosphine)cobalt(II). A quantity of 5 g (21 mmole) of CoCl₂ · 6 H₂O in *n*-butanol and 10.25 g (42 mmole) of *n*-butyl-diphenylphosphine, also in *n*-butanol, were combined under nitrogen and the resulting blue precipitate was recrystallized from *n*-butanol. Anal.: Calc. for CoCl₂[P(*n*-C₄H₉)(C₆H₅)₂]₂: C, 62.54; H, 6.23; Cl, 11.54. Found: C, 62.61; H, 6.36; Cl, 11.62.

Dichlorobis(di-n-butylphenylphosphine)cobalt(II). Solutions of 8.5 g (35.5 mmole) of CoCl₂ · 6 H₂O in ethanol and 11.85 g (70 mmole) of di-*n*-butylphenylphosphine were combined and upon cooling in dry ice a blue precipitate was formed. The crystals were recrystallized from *n*-butanol. Anal.: Calc. for CoCl₂[P(*n*-C₄H₉)₂(C₆H₅)₂]₂: C, 58.54; H, 8.07; Cl, 12.34. Found: C, 58.73; H, 8.17; Cl, 12.59.

Apparatus. The instrument used for the thermogravimetric measurements was an Aminco Thermo-Grav manufactured by the American Instrument Company, Silver Springs, Md. The sample size was about 200 mg, the sweep gas in all cases, except where noted, was a mixture of 10% oxygen and 90% helium at a flow rate of 50 cc per minute, the heating rate was 3° per minute. After a completed run the residue left in the crucible of the apparatus was re-weighed and the overall weight loss thus determined agreed well with the weight loss recorded by the thermobalance.

Results and discussion

Cobalt(II) halide complexes with monodentate phosphines have been shown to have pseudo tetrahedral d^7 structure [9]. Also, in the monochelate compound $\text{CoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ pseudo tetrahedral coordination is involved [6]. However, for the dichelate compound $\text{CoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ a pentacoordinated structure has been suggested [6]. The triphenylphosphine oxide complexes also are pseudo tetrahedral.

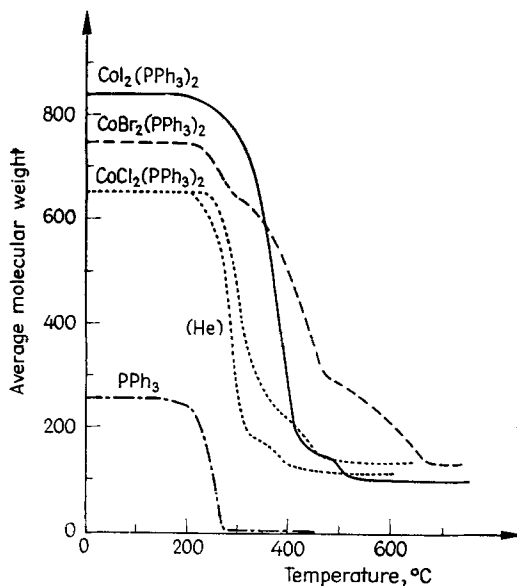


Fig. 1. Thermogravimetric curves of cobalt(II)halide bistrisphenylphosphine complexes, $\text{CoX}_2(\text{PPh}_3)_2$

Triphenylphosphine complexes. As shown in Fig. 1, the bistrisphenylphosphine complexes of cobalt(II) halides appear to decompose in the neighborhood of ca. 255° in an oxygen containing atmosphere. Although no significant difference in the initial decomposition temperature for the three halides seems to occur, there are differences in the decomposition rates. The average molecular weight of the residue upon reaching the horizontal part of the weight loss curve ranges from 110 for the iodide, to 131 and 139 for the bromide and chloride respectively. This residue does not contain halogen as would be expected but cobalt and phosphorus. A typical analysis resulted in 47.4% cobalt and 18.2% phosphorus with X-ray diffraction patterns of this residue indicating the presence of Co_3O_4 and $\text{Co}_3(\text{PO}_4)_2$ and perhaps other components as evidenced by several diffraction lines which could not be assigned to previously recorded patterns. Pure cobalt halide, however, is obtained as the residue when the thermal decomposition of these complexes is performed in an atmosphere of dry helium.

These results lead to the conclusion that under the above conditions part of the triphenylphosphine is oxidized to phosphate. In the case described above, 0.7 mole of the two moles of phosphorus present in the complex as triphenylphosphine were oxidized. Since a sample of pure triphenylphosphine under identical conditions cleanly distilled out of the crucible of the TGA apparatus in the range from 150 to 270° without generating a non-volatile residue, the observed oxidation in the case of the complexes must be due to catalysis by cobalt ions. Concurrent with this process the initially resulting uncoordinated cobalt halide — probably as a result of its involvement in the oxidation process — reacted with the generated water to form the observed cobalt oxides. Anhydrous cobalt halides in an anhydrous atmosphere are thermally quite stable, e.g., cobalt dichloride is reported to melt at 735°.

The initial decomposition temperature of the complexes as determined from the curves in Fig. 1 truly represents the temperature at which the coordinated triphenylphosphine is released from the central atom since this process occurs at a higher temperature than the temperature at which initial distillation of triphenylphosphine is observed under comparable conditions. The thermogravimetric curves also show that once the thermal degradation of the complex is initiated, no stable stoichiometric intermediates are realized, such as perhaps a monophosphine complex.

In contrast to these studies the thermal stability of cobalt ammine complexes, e.g., $\text{Co}(\text{NH}_3)_6\text{X}_2$ is dependent on the ligand X and generally increases in the order fluoride < chloride < bromide < iodide [1]. Fig. 1 shows that no such stability relationship exists for the triphenylphosphine complexes of cobalt.

Other phosphine complexes. In Fig. 2 thermogravimetric curves are presented for cobalt(II) halide diphosphine complexes with the phosphine ligands being members of the series $\text{P}(n\text{-C}_4\text{H}_9)(\text{C}_5\text{H}_5)_2$, $\text{P}(n\text{-C}_4\text{H}_9)_2(\text{C}_6\text{H}_5)$ and $\text{P}(n\text{-C}_4\text{H}_9)_3$. The data show that the thermal stability of the complexes $\text{CoCl}_2[\text{P}(n\text{-C}_4\text{H}_9)_n(\text{C}_6\text{H}_5)_{3-n}]$ decreases with increasing n . Although one would expect that owing to the stronger basicity of aliphatic substituted phosphines, complexes of the latter should be thermally more stable than those of aromatic phosphines. In view of the complexity of the bonding between cobalt and phosphorus involving back bonding contributions such a simple relationship does not appear to exist.

The complexes involving the chelating diphosphine, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, appear to be more stable thermally than the ones involving coordination of monophosphines. However, in view of the low volatility of the chelating ligand itself under comparable conditions the thermogravimetric data in this case do not permit an unequivocal decision as to the thermal stability of the complex. The temperature at which initial weight loss of the complex is observed, is in about the same range as that for the volatilization of the ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ when run under comparable conditions. Therefore, the decision whether the observed weight loss curve in this case is determined by the volatility of the ligand which might have dissociated long before weight loss is recorded, or whether the curve truly represents a thermal dissociation process of volatile components cannot

be made based on the present data alone. The extremely high melting point at 350—354° observed for the chelated complex $\text{CoCl}_2[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]$, however, is indicative of the high thermal stability of this compound. This argument, on the other hand, does not apply to the complex $\text{CoCl}_2[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]_2$ as evidenced by its low melting point and visually observable decomposition point. This complex degrades long before weight loss is seen in the thermogravimetric curve.

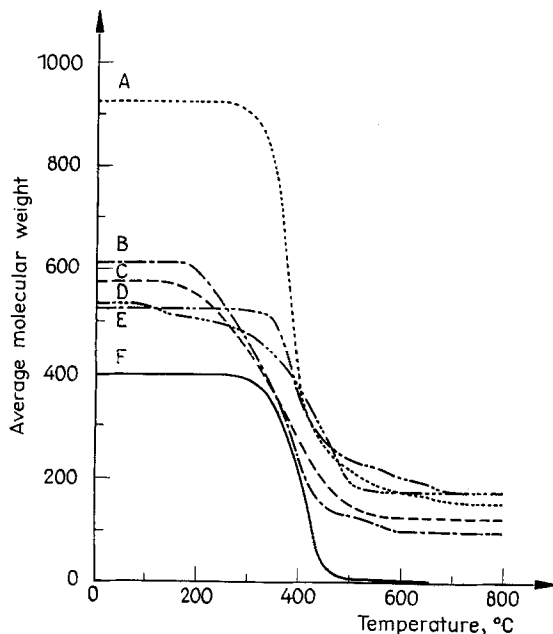


Fig. 2. Thermogravimetric curves of some cobalt(II) chloride phosphine complexes, $\text{CoCl}_2(\text{PR}_3)_2$
 A: $\text{CoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ B: $\text{CoCl}_2(\text{PPh}_2\text{Bu})_2$
 C: $\text{CoCl}_2(\text{PPhBu}_2)_2$ D: $\text{CoCl}_2(\text{PBu}_3)_2$ E: CoCl_2
 $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ F: $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$

Also these complexes when heated in an oxygen containing atmosphere yield residues the molecular weights of which range from ca. 100 to 175 and which do not contain chlorine. These are solid phases consisting of Co_3O_4 and P_2O_5 and compounds between those two species.

Triphenylphosphine oxide complexes. In phosphine oxide coordination can take place only through oxygen. Therefore, the triphenylphosphine oxide complexes of cobalt(II) halides are not of the same class as the complexes discussed in the above part of the paper. Since the thermal decomposition of some of the phosphine complexes might very well proceed via intermediate phosphine oxide complexes it was of interest to include these in the present investigation.

As shown in Fig. 3, the chloride and bromide complexes both start to decompose at about 250° which is not very far off from where the analog triphenylphosphine complexes were observed to experience weight loss. The iodide complex appears to be less stable, decomposition is seen to start at about 200°. The rate at which weight loss occurs is much faster for the iodine than for the chlorine or bromine compound. When the curves in Fig. 3 for the complexes are compared

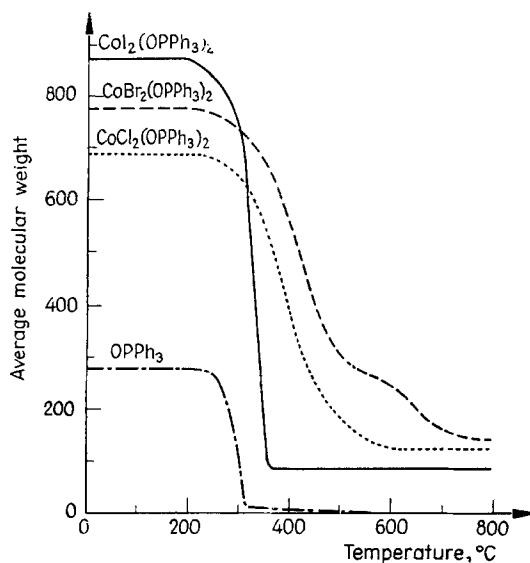


Fig. 3. Thermogravimetric curves of cobalt(II) halide bistrisphenylphosphine oxide complexes, $\text{CoX}_2(\text{OPPh}_3)_2$

with the one for the ligand triphenylphosphine oxide obtained under comparable conditions, it becomes obvious that the data do not permit the conclusions that the temperature at which weight loss is first observed is also the decomposition temperature. The initial weight loss pattern of triphenylphosphine oxide distilling out of the sample holder is quite similar to the ones observed for the complexes. Since the melting points of the compounds of Fig. 3 lie within the same temperature range where weight loss is seen to occur it may be assumed quite reasonably that dissociation of the coordinated triphenylphosphine oxide takes place at or near the melting point.

The average apparent molecular weight of the residues of the thermal decomposition of the triphenylphosphine oxide complexes ranges from 80 for the iodide to 126 for the chloride and 143 for the bromide. Again, the composition of these is interpreted in terms of various solid phases involving Co_3O_4 , $\text{Co}_3(\text{PO}_4)_2$ and P_2O_5 which were generated by cobalt catalyzed oxidation processes. The residue obtained by thermally decomposing $\text{CoCl}_2(\text{OPPh}_3)_2$ analyzed as 50.0% cobalt and 16.4% phosphorus with no detectable halogen.

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RÉSUMÉ — On a étudié la décomposition thermique des complexes dihalogénés de cobalt(II) avec les aryl et alcoylphosphines substituées et les oxydes de triphénylphosphine. En atmosphère d'oxygène, Co_3O_4 et P_2O_5 constituent la phase solide résiduelle.

ZUSAMMENFASSUNG — Komplexe von Kobalt(II)dihalogeniden mit aryl- und alkylsubstituierten Phosphinen und Triphenylphosphinoxyd wurden einer thermogravimetrischer Prüfung unter Sauerstoff unterworfen. Die zurückbleibende feste Phase bestand aus Co_3O_4 und P_2O_5 .

Резюме — Измерения, проведенные методом дериватографии, показали, что разложение комплексов галогенидов кобальта с фосфинами и окисями трифенилфосфина замещенными арил- и алкил-группами, в атмосфере, содержащей кислород, приводит к образованию твердой фазы, состоящей из смеси окисей Co_3O_4 и P_2O_5 .