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ΓHERMAL DECOMPOSITION OF Cu(I) PHOSPHINE COMPLEXES

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The thermal decomposition of Cu(I) phosphine complexes of the general types $(CuXPPh_3)_4$, $[CuX(PPh_3)_2]$ and $[CuX(PPh_3)_3]$ was investigated.

The thermal decomposition of $(CuXPPh_3)_4$, where X denotes Cl^-, Br^-, I^-, NO_3^- and $PPh_3 = P(C_6H_5)_3$, occurs with formation of a phosphine oxide intermediate. For the remaining complexes this intermediate was not proved in the thermal decomposition.

Great attention has recently been paid to the study of the thermal decomposition of phosphine complexes with various transition metals [1].

The study of the Ni(II), Co(II) and Pd(II) complexes of the type $[M(PR_3)_2X_2]$, where $M = Ni^{II}$, Co^{II} and Pd^{II}, PR_3 denotes a tertiary phosphine and X^- an inorganic anion, has shown that with increasing temperature an oxygen atom is inserted into the M—P bond, with formation of phosphine oxide or $[M(OPR_3)_2X_2]$ complex.

The phosphine complexes of univalent copper might serve as very interesting experimental materials for study of the analogous reaction:

a) with increasing temperature some decrease in stability of Cu(I) compounds may be expected;

b) complexes of various types, such as $(CuXPPR_3)_4$, $[CuX(PPR_3)_2]$, $[CuX(PPR_3)_3]$ and $[Cu_2X_2(PPR_3)_3]$ may be prepared [2, 3];

c) the influence of the anion on the course of thermal decomposition for the given type of compound may be studied. To the best of information, such a systematic investigation of the thermal decomposition of Cu(I) complexes has not been performed to date.

Experimental

Cu(I) complexes were synthesized from analytically pure substances. Before use, triphenylphosphine was recrystallized from ethanol (melting point 79°).

Phosphorus determination was performed using the method of Marie [4]; the halogens were determined using the method of Schöniger [5]; and copper was weighed after its ignition to CuO.

The thermal decomposition was studied on a derivatograph (MOM, Budapest) with sample weights in the range 120—140 mg at a heating rate of 2.5°/min. The infrared absorption spectra were recorded in nujol on a Specord IR 75 (Zeiss, Jena) instrument and the magnetic susceptibility was measured at 25° by the Gouy method, using the magnetobalance constructed by the Development Laboratories and workshops of Palacký University. For calibration $Hg[Co(CNS)_4]$ was applied.

Results and discussion

The phosphine complexes were prepared *via* described methods [3, 6, 7]; their compositions are given in Table 1. All isolated compounds were diamagnetic, which indicates the absence of copper(II).

On the basis of the course of the thermal decomposition, the investigated complexes may be divided into two groups (Table 2). Those belonging to the first group include the compounds of general formula $(CuXPPh_3)_4$, where $X^- = Cl^-$, Br^-, I^- and NO_3^-. The TG curves of these compounds (Fig. 1) reveal some weight increase over 150°, this being accompanied by a sharp exotherm in the DTA curve. The further course of the TG curve indicates the decomposition of this intermediate. This latter decomposition takes place without the formation of a definite or perceptible intermediate. To clarify the intermediate increase in weight, $(CuClPPh_3)_4$ was heated isothermally for two hours at $(150 \pm 1)°$ (at which temperature the maximum of the exothermic process appears in the DTA curve of this compound). The analytical results on the substance produced in this way correspond closely to the formula $CuCl \cdot OPPh_3$. This substance is diamagnetic, which

Table 1

Analysis of compounds

Compound	Theoretical			Experimental		
	% Cu	% P	% X	% Cu	% P	% X
$Cu(PPh_3)Cl$	17.59	8.57	9.81	16.95	9.14	9.82
$Cu(PPh_3)Br$	15.66	7.63	19.64	15.80	7.47	19.79
$Cu(PPh_3)I$	14.03	6.84		14.18	6.54	
$Cu(PPh_3)NO_3$	16.38	7.99		16.88	8.17	
$Cu(PPh_3)CNS$	16.55	8.06		16.66	8.27	
$Cu(PPh_3)CN$	18.05	8.80		18.55	8.52	
$Cu(PPh_3)_2Cl$	10.19	9.93	5.69	10.53	10.15	5.86
$Cu(PPh_3)_2Br$	9.51	9.27	11.96	10.03	8.96	12.05
$Cu(PPh_3)_3Cl$	7.17	10.49	4.00	7.42	10.22	4.15
$Cu(PPh_3)_3Br$	6.83	9.99	8.59	6.69	9.88	8.79
$Cu(PPh_3)_3I$	6.50	9.51		6.71	9.09	

$X = Cl^-, Br^-$

Table 2

Temperature of beginning of weight change and DTA peak temperature of Cu(I) complexes

Compound	$+\Delta m$, temp. °C	Exothermic peak temp., °C	$-\Delta m$, temp. °C	Endothermic peak temp., °C
$CuClPPh_3$	125	150	245	225
$CuBrPPh_3$	170	180	240	220
$CuIPPh_3$	—	190	190	—
$Cu(NO_3) \cdot PPh_3$	140	205	225	270
$Cu(CNS) \cdot PPh_3$	—	—	200	215
$Cu(CN) \cdot PPh_3$	—	—	215	215
$Cu(PPh_3)_2Cl$	—	—	135	155
$Cu(PPh_3)_2Br$	—	—	145	175, 185
$Cu(PPh_3)_3Cl$	—	—	165	175
$Cu(PPh_3)_3Cl$	—	—	145	175, 185
$Cu(PPh_3)_3I$	—	—	140	145

would suggest that no copper oxidation has yet taken place. In the IR absorption spectrum the pronounced maximum appears near 1180 cm^{-1}, which corresponds [8, 9] with the ν_{P-O} stretching vibration. This maximum was found in the IR spectra of the other compounds of this group which had been treated in an analogous way, i.e. they were heated for two hours to the temperature at which an exothermic peak appears in their DTA curve. This maximum does not appear in the

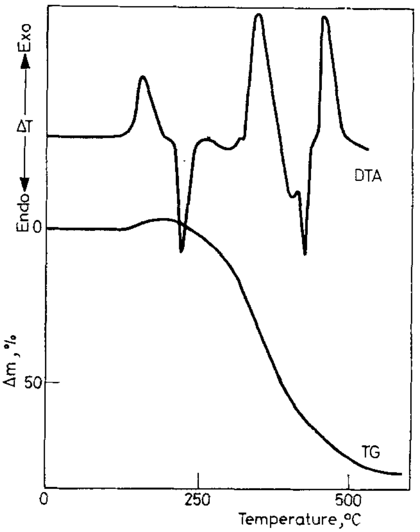

Fig. 1. DTA and TG curves of $(CuClPPh_3)_4$

IR spectra of the starting complexes. From these results it may be concluded that, on being heated, the phosphine complexes are converted into complexes of phosphine oxide; this change, however, as may be seen from the TG curve, is not a quantitative one. With increase of the temperature or with lengthening of the isothermal heating, decomposition of the intermediates begins. From Table 2 it is evident that the temperature at which the reaction of aerial oxygen with the phosphine complex starts increases in the following order: chloride < bromide < < iodide. In the case of the iodide, an exothermic peak is observed in the DTA curve, but it lies at such a high temperature that formation of the intermediate is overlapped by its thermal decomposition.

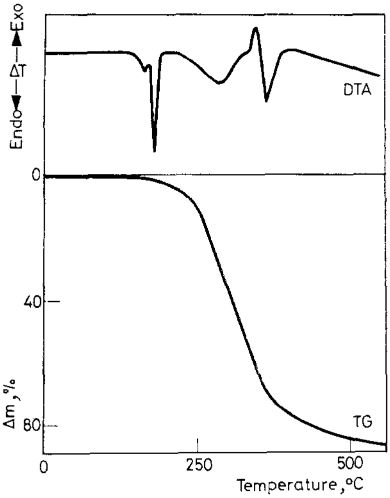

Fig. 2. DTA and TG curves of [Cu(PPh$_3$)$_3$)Cl]

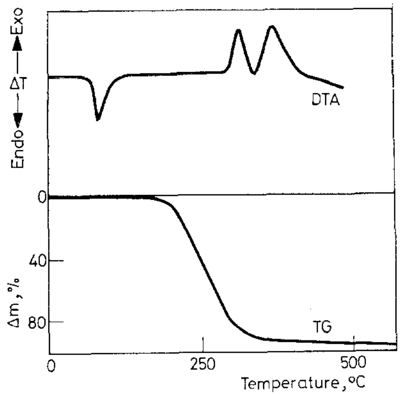

Fig. 3. DTA and TG curves of PPh$_3$

The remaining compounds may be classed in the second group; these undergo thermal decomposition without perceptible formation of the phosphine oxide intermediate (Fig. 2). The course of thermal decomposition of triphenylphosphine alone is given in Fig. 3. It is evident that at 80° an endotherm corresponding to the melting point appears, followed from 135° by thermal decomposition without the formation of a definite intermediate. The present results allow the conclusion that the transition of triphenylphosphine to triphenylphosphine oxide proceeds only in the thermal decomposition of certain phosphine complexes. In the set of complexes studied in this article, these were compounds in which only one triphenylphosphine and anion were bound to the central atom, these not being suitable for the stabilization of the Cu(I) state, i.e. Cl^-, Br^- and NO_3^-.

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Résumé — On a étudié la décomposition thermique des complexes phosphine-Cu(I) de formule générale $(CuXPPh_3)_4$, $[CuX(PPh_3)_2]$, $[CuX(PPh_3)_3]$. La décomposition thermique de $(CuXPPh_3)_4$, où X désigne Cl^-, Br^-, I^- et NO_3^-, et $PPh_3 = P(C_6H_5)_3$, s'effectue avec formation d'un oxyde de phosphine intermédiaire; avec les autres complexes, cet intermédiaire n'a pas été mis en évidence au cours de la décomposition thermique.

Zusammenfassung — Die thermische Zersetzung der Cu(I)-Phosphinkomplexe vom allgemeinen Typ $(CuXPPh_3)_4$ und $[CuX(PPh_3)_2]$, wie auch $[CuX(PPh_3)_3]$ wurde untersucht. Die thermische Zersetzung von $(CuXPPh_3)_4$, wobei $X = Cl^-$, Br^-, I^- und NO_3^- bedeutet und $PPh_3=P(C_6H_5)_3$, verläuft unter Bildung eines Phosphinoxid Zwischenproduktes, bei den übrigen Komplexen konnte dieses im Laufe der thermischen Zersetzung nicht nachgewiesen werden.

Резюме — Исследовано термическое разложение комплексов фосфина с одновалентной медью общей формулы $(CuXPPh_3)_4$ $[CuX(PPh_3)_2]$ и $[CuX(PPh_3)_3]$. Термическое разложение комплексов типа $(CuXPPh_3)_4$, где $X = Cl^-$, Br^-, I^-, NO_3^-, и $PPh_3 = P(C_6H_5)_3$ происходит с образованием окиси фосфина как промежуточного продукта. При термическом разложении оставшихся комплексов образование окиси фосфина не установлено.