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THERMAL STUDIES ON PALLADIUM ALKYL XANTHATES

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ABSTRACT

Eleven palladium(II) alkylxanthates, $Pd(ROCSS)_2$ [R = Me, Et, nPr, iPr, nBu, iBu, tBu, nAm, iAm, nHex and cyclohex], have been prepared and their thermal properties investigated by thermogravimetric analysis. The complexes, although volatile under vacuum (10^{-2} mm Hg), decompose without volatilization at normal atmospheric pressure leaving a residue of palladium metal at 950°C. The intermediate decomposition products were identified mass spectrometrically and a thermal decomposition mechanism is proposed.

INTRODUCTION

Thermal investigations on metal dithiocarbamates and xanthates have not been numerous. In the case of the former, Bernard and Borel[1] carried out a thermochemical study using thermogravimetry and differential thermal analysis on the dithiocarbamates of lead, zinc and cadmium. D'Ascenzo and Wendlandt[2] determined the thermal properties of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and mercury(II) complexes of diethyl-dithiocarbamic acid using thermogravimetry, differential thermal analysis, and high temperature reflectance spectroscopy, and the same authors[3] reported TG, DTA, and vapour pressure studies on iron(II) diethyldithiocarbamate.

Reports on the thermal properties of metal xanthates have been even fewer. Fackler *et al.*[4], examined some nickel(II) xanthates and claimed that olefin formation occurs when they are thermally decomposed. Recently, Cavell *et al.*[5] reported thermal studies on eleven nickel alkyl xanthates and proposed a thermal decomposition mechanism involving carbonyl sulphide, the formation of nickel sulphide, and the presence of S-ethyl O-ethyl xanthate as a stable intermediate.

This paper reports thermogravimetric analysis data for eleven palladium alkyl xanthates, $Pd(ROCSS)_2$ [R = Me, Et, nPr, iPr, nBu, iBu, tBu, nAm, iAm, nHex and cyclohex]. A thermal decomposition mechanism is proposed.

EXPERIMENTAL

Preparation of palladium alkyl xanthates

The potassium salts of the appropriate xanthate ligand were prepared as described by Vogel[6]. They were re-crystallised from acetone/ether and washed with ether.

The palladium alkyl xanthate complexes were prepared by adding an aqueous solution of analar grade palladous chloride to an aqueous solution containing a slight excess of ligand. The complexes were filtered and washed several times with water and then dried in vacuo over P_2O_5. They were all re-crystallised from chloroform and dried in a vacuum desiccator for several days. Sublimation followed and the sublimed material was used for further experimental work.

All the complexes sublimed at reduced pressure (approx. 10^{-2} mm Hg). The degree of volatility was found to depend on the alkyl group, the most volatile being the *n*-propyl, i-propyl, n-butyl, and i-butyl derivatives.

Micro-analyses for C, H, and S were carried out on the palladium complexes by the CSIRO Microanalytical Service, Melbourne University. The palladium content of the complexes was determined thermogravimetrically as palladium metal at 950 °C.

The elemental analyses for the palladium methyl-, ethyl-, n-butyl-, n-amyl-, n-hexyl- and cyclohexyl-xanthates are reported in Table 1. They are typical of the

TABLE 1

MICRO-ANALYSES OF PALLADIUM XANTHATES

Compound	*Formula*		*C*	*H*	*S*	*Pd*
$(MeXan)_2Pd$	$C_4H_6O_2S_4Pd$	Found	15.0	1.9	36.6	32.9
		Calcd.	15.0	1.9	40.0	33.2
$(EtXan)_2Pd$	$C_6H_{10}O_2S_4Pd$	Found	20.8	2.8	36.9	30.2
		Calcd.	20.7	2.9	36.7	30.5
$(nBuXan)_2Pd$	$C_{10}H_{18}O_2S_4Pd$	Found	30.1	4.4	30.6	26.2
		Calcd.	29.7	4.4	31.6	26.3
$(nAmXan)_2Pd$	$C_{12}H_{22}O_2S_4Pd$	Found	3[illegible].5	5.1	27.6	24.9
		Calcd.	33.3	5.1	29.6	24.6
$(nHexXan)_2Pd$	$C_{14}H_{26}O_2S_4Pd$	Found	36.6	5.4	27.0	23.1
		Calcd.	36.5	5.6	27.8	23.1
$(cyclohexXan)_2Pd$	$C_{14}H_{22}O_2S_4Pd$	Found	36.6	4.8	27.6	—
		Calcd.	36.8	4.8	28.0	—

TABLE 2

MELTING POINTS OF PALLADIUM XANTHATES

Compound	*M.P. (°C)*	*Ref. value (°C)*	*Ref.*
$(MeXan)_2Pd$	145 decomposes	140 decomposes	7
$(EtXan)_2Pd$	151	152	7
$(nPrXan)_2Pd$	126	126–127	7
$(iPrXan)_2Pd$	138	—	—
$(nBuXan)_2Pd$	116	—	—
$(iBuXan)_2Pd$	126	—	—
$(tBuXan)_2Pd$	147	—	—
$(nAmXan)_2Pd$	91	—	—
$(iAmXan)_2Pd$	116	—	—
$(nHexXan)_2Pd$	81	—	—
$(cyclohexXan)_2Pd$	174 decomposes	—	—

others and show satisfactory agreement with predicted values confirming a high degree of purity. Melting points are recorded in Table 2.

Thermograms were obtained using a Stanton Thermobalance (Model TR-01) with an air furnace atmosphere. Sample sizes of 50 mg were used at the conventional furnace heating rate of 4 °C per minute.

Volatility studies

These were carried out in all cases in a vacuum of better than 0.01 mm Hg. The vacuum was measured approximately on an Edwards Vacustat.

RESULTS AND DISCUSSION

In Fig. 1, the thermograms for each complex are reproduced. Decomposition starts, depending on the derivative, over a wide range of temperature, *e.g.*, palladium

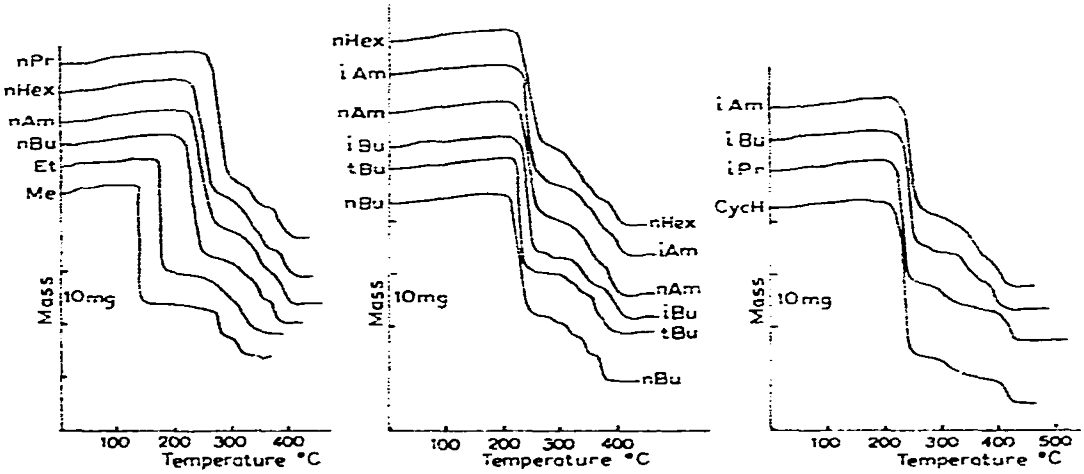


Fig. 1. Main decomposition step for palladium alkylxanthates.

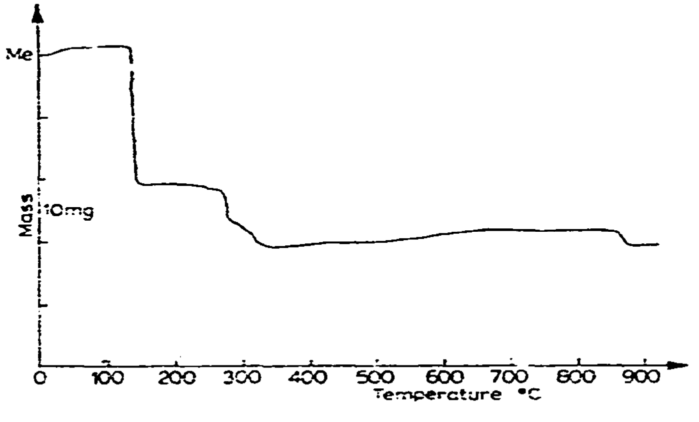


Fig. 2. Mass-loss curve of $Pd(MeXan)_2$ in air.

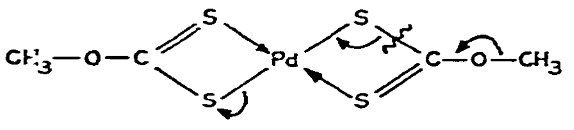
methyl xanthate, 135°C; and palladium n-propyl xanthate, 250°C. In general, the first decomposition step in each thermogram is associated with a rapid loss in weight in which the major part of the molecule is lost. This is followed by a much slower decomposition step, in which there is evidence of a two step breakdown. A long plateau follows up to approximately 900°C (Fig. 2), but in the middle of this plateau around 500–600°C there is indication of a very small increase in weight, possibly due to partial oxidation of the palladium metal. This is followed by a small weight loss and a constant weight plateau representing the formation of metallic palladium.

Thermal decomposition mechanism

To investigate the mechanism of thermal decomposition in detail, palladium methyl xanthate was selected as representative of the group. The thermogram of this complex (Fig. 2), shows a stable plateau from 150–250°C.

A 1.0 g sample of palladium methyl xanthate in a round-bottomed flask was heated in a silicone-oil bath. The complex decomposed at 135°C. A malodorous gas was given off and a clear liquid condensed on the cool parts of the flask. Both the gaseous and liquid fractions were collected and analysed by the mass spectrometer. The gaseous fraction showed one strong mass peak at m/e = 60, indicative of COS (carbonyl sulphide): no other mass peak was observed in the mass spectrum. The clear liquid fraction showed a strong parent peak at m/e 122. This indicated the presence of S-methyl, O-methyl xanthate ($CH_3{-}O{-}\underset{\underset{S}{\|}}{C}{-}S{-}CH_3$).

Other peaks, which appear to represent the breakdown of this intermediate, were also present in the mass spectrum. From these mass spectrometric results it would appear that a thermal decomposition mechanism, similar to that of nickel alkyl xanthates[5] might be envisaged, as follows:



$$\rightarrow CH_3{-}O{-}\underset{\underset{S}{\|}}{C}{-}S^- + CH_3^+ + PdS + COS$$

$$\rightarrow CH_3{-}O{-}\underset{\underset{S}{\|}}{C}{-}S{-}CH_3 + PdS + COS.$$

One difficulty, however, arises with this interpretation. In Fig. 2 the initial weight-loss step for palladium methyl xanthate corresponds to a loss of weight of 22.5 mg, whereas, on the basis of the above proposed mechanism, a weight-loss of 28.5 mg is required.

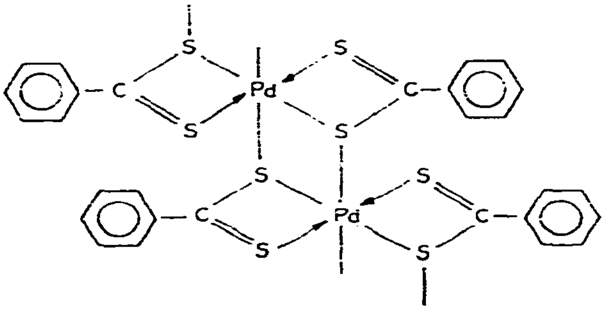
In an attempt to clarify the situation, a sample of the residue, obtained after heating to 135–140°C, was washed with chloroform to remove any extraneous organic matter (the residue itself is insoluble in chloroform) and finally analysed. Element analysis figures on a number of samples gave the following average values: C, 8.1; H, 1.8; S, 29.3; Pd, 59.5%.

There was no evidence for any other element being present in the compound. The analysis obtained corresponds to an empirical formula of $Pd_2C_2H_6S_3$.

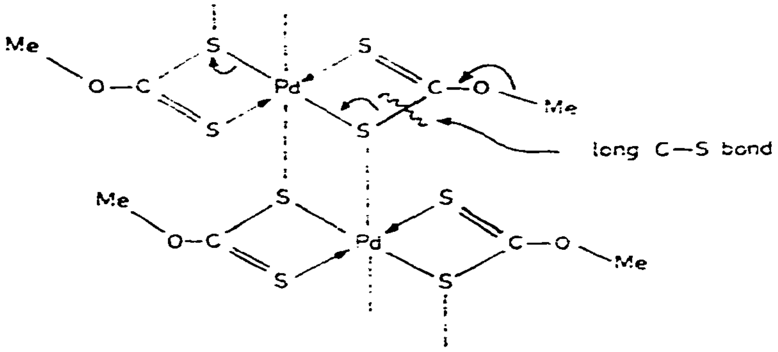
To take the proposed mechanism a stage further, it is necessary to examine the complex in the crystalline form. However, the crystal structure of this compound has never been carried out. Use was, therefore, made of Franzini's results[9] for nickel ethyl xanthate and Bonamico and Dessy's work[10] on palladium dithiobenzoate.

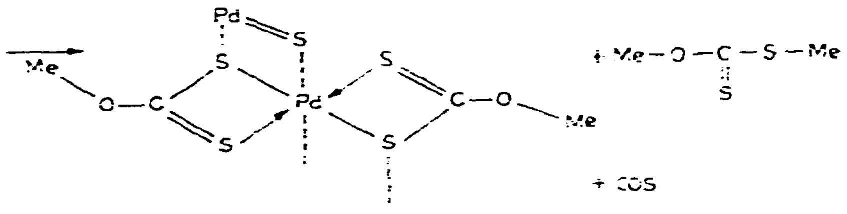
In the former, it was shown that the whole molecule is planar and that one C–S bond is longer than the other due to interaction of the nickel atom with sulphur atoms in a neighbouring molecule. It is expected that in the thermal breakdown, this longer bond will break first.

In Bonamico and Dessy's picture of the crystal structure of palladium bis-dithiobenzoate (a compound similar in structure to alkyl xanthates), there is interaction between the palladium atom and the sulphur atoms of an adjoining molecule.

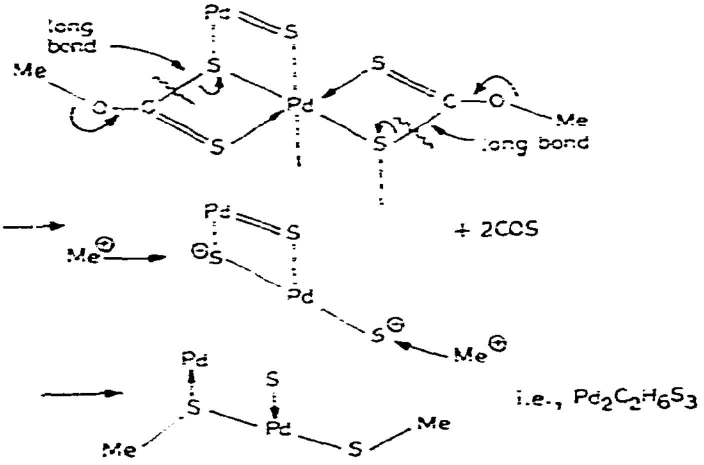


On the basis that the long C–S bond breaks first, an amended mechanism is proposed:
(A) A long C–S bond breaks similar to nickel xanthate[5] giving COS and S-methyl O-methyl xanthate





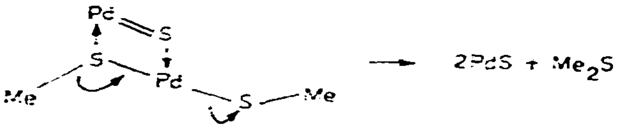
(B) Two more long C–S bonds break to give two additional molecules of COS



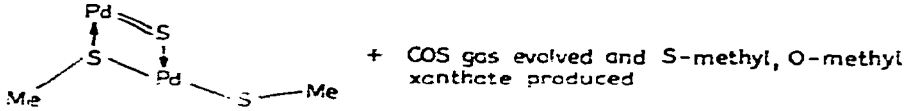
Analysis figures for the above complex are as follows:

Found: C, 8.1; H, 1.8; S, 29.3;
Calcd: C, 7.1; H, 1.8; S, 28.3.

The complex above, $Pd_2S_3Me_2$, was found to be insoluble in all the solvents tested. On standing in air, it slowly evolves a vapour of characteristic odour. This was collected and analysed by the mass spectrometer. It was found to be pure dimethyl sulphide, Me_2S. Thus, the intermediate palladium species undergoes breakdown as follows



On the basis of the above results, the thermogram for palladium methyl xanthate can be resolved (Fig. 1) into the following steps:
Stage 1. Decomposition starts at 135 °C and a rapid loss of weight occurs (A). The product at the end of this step is the intermediate species



Stage II. After a constant weight plateau between 140–250 °C, the intermediate species undergoes decomposition with the evolution of dimethyl sulphide Me_2S, leaving at the end of step (B), PdS.
According to Duval[11], PdS decomposes above 220 °C yielding palladium metal.
Stage III. This is represented by region (C) in Fig. 2 and indicates the decomposition of PdS, leaving Pd metal as a final non-degradable residue.
In the thermogram of palladium methyl xanthate, as with the other complexes, a slight increase in weight takes place above 550 °C, a constant weight level exists over the temperature range 625–870 °C after which a further weight loss occurs leading to a final constant weight level at 950 °C. The increase in weight at 550 °C is thought to be due to partial oxidation of the metal and, at higher temperature, the metal is produced again.

From the thermograms of the other palladium xanthates (R = Et→cyclohex), it seems plausible that they follow the same decomposition mode. The slight differences in the curves can be accounted for by the fact that the decompositions occur at a higher temperature, and that at these temperatures the intermediates thus formed, decompose rapidly. Consequently, no stable plateaus are formed.

From the thermograms, some general conclusions about the effect of the terminal alkyl groups on the thermal properties of the respective complexes can be drawn. Three trends are evident:

(i) as the chain length of the R-group increases, the temperature of breakdown increases (with the exception of the n-propyl complex which is the most stable complex),
(ii) as the chain length increases, the decomposition rate decreases, *i.e.*, slope in stage I becomes more horizontal,
(iii) as branching increases, the decomposition rate increases.

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