

THERMAL DECOMPOSITION OF PALLADIUM COMPLEXES WITH PROPYLENEDIAMINETETRAACETIC ACID

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ABSTRACT

Thermal decomposition processes of several palladium complexes with propylenediaminetetraacetic acid (PDTA- H_4) have been studied using DTA, TG and DTG techniques. Intermediate products in the decomposition processes were characterized by IR spectroscopy. For all the compounds, decarboxylation proceeds in two stages, free carboxylic groups being lost in the first step and coordinated carboxylate groups in the second. For the complexes containing ethylenediamine and thiocyanate, the processes are complicated by the presence of these ligands. PdO has been detected as the final product in the decomposition processes, although in the complex $[Pd_2(CNS)_2(PDTA-H_2)] \cdot 2 H_2O$, $PdSO_4$ is also formed.

INTRODUCTION

Differential thermal analysis (DTA) and thermogravimetry (TG) have been widely used for the study of the thermal decomposition of coordination compounds with propylenediaminetetraacetic acid (PDTA- H_4). Thus, for the case of several palladium complexes [1], it has been established that the water of crystallization is lost between 100 and 150°C, and the combustion of the organic material occurs between 200 and 450°C.

Nevertheless, the results obtained by applying only these techniques do not permit the determination of the sequence in which the several groups of the complex are released. So, it is necessary to use an auxiliary technique in order to obtain new data and to solve in some way the complexity of the processes which are taking place. In this way, the chromatographic analysis of the gases evolved in the thermal process has been recently applied in our laboratories for the study of several polycarboxylic chelating ligands [2,3]. For these compounds, we observed that decarboxylation of free carboxylic groups occurs first followed by that of the neutralized groups at a higher temperature. This different behaviour must be accentuated in the coordination compounds, where decarboxylation must occur in at least two stages.

In this paper, the validity of the preceding assumption is verified for the

case of several palladium complexes with PDTA. Infrared spectroscopy has been successfully applied as an auxiliary technique for the study of the decomposition processes.

EXPERIMENTAL

The synthesis of the complexes has been reported in a previous paper [4]. DTA and TG curves were obtained using a Mettler TA-HE-20 system with Pt/Pt 10% Rh thermocouples. α - Al_2O_3 was used as reference material in the DTA measurements. The heating rate was $10^\circ\text{C min}^{-1}$ in all cases. DTG curves were obtained by connecting a Mettler TA-50 derivatograph to the system. When the experiments were carried out in an atmosphere of argon, the flow rates were 300 ml min^{-1} (balance) and 30 ml min^{-1} (furnace). Infrared spectra of solid intermediate products were recorded in KBr pellets using a Pye Unicam SP3-300 spectrophotometer.

RESULTS AND DISCUSSION

Thermal decomposition of $[\text{Pd}(\text{PDTA-H}_3)\text{Cl}] \cdot 2 \text{H}_2\text{O}$

The DTA and TG curves obtained for this compound in an atmosphere of static air are given in Fig. 1. There is an initial weight loss of 9% associated with an endothermic effect at 150°C , both corresponding to the elimination of the water of crystallization, as shown in Fig. 2 by the disappearance of the $\nu_{\text{O-H}}(\text{H}_2\text{O})$ band in the IR spectra of heated samples. The theoretical value for the elimination of two water molecules is 7.45%.

Between 200 and 400°C there is a great weight loss associated with weak thermal effects in the DTA curve. This step overlaps the other one of greater slope occurring between 400 and 500°C which is associated with the great exothermic effect with maximum at 450°C . Because this last effect is not observed when the experiment is carried out in an atmosphere of argon, we associate it with the combustion of the organic material. The inert atmosphere also modifies to a great extent the DTA curve at lower temperatures, two endothermic effects appearing at 210 and 240°C , and the effect corresponding to the loss of water being displaced to 125°C . Nevertheless, the total weight loss is the same as that obtained in air (82%), suggesting that the final product is the same in both cases.

The DTG curve permits several overlapping steps in the weight loss between 200°C and the combustion of the organic material to be distinguished. Infrared spectra (Fig. 2) show that free carboxylic groups are released in the first step (200 – 220°C), because the strong band centered at 1700 cm^{-1} gradually loses intensity and disappears. Although in the TG

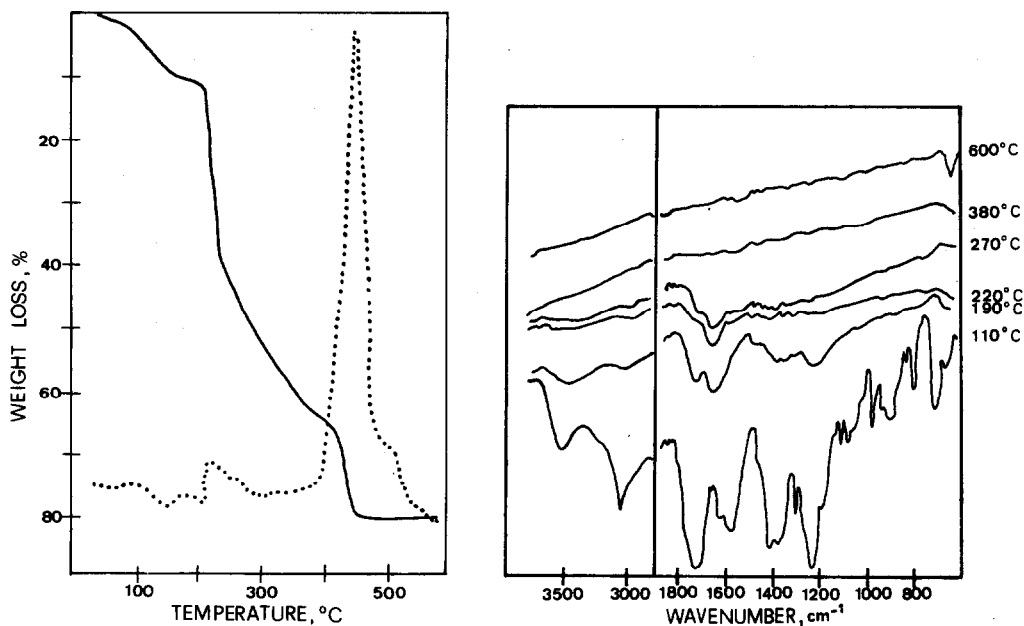


Fig. 1. DTA and TG curves for $[\text{Pd}(\text{PDТА-H}_3)\text{Cl}] \cdot 2 \text{H}_2\text{O}$ in an atmosphere of static air.

Fig. 2. IR spectra of some intermediate products in the decomposition of $[\text{Pd}(\text{PDТА-H}_3)\text{Cl}] \cdot 2 \text{H}_2\text{O}$.

curve the weight loss corresponding to this step is over 23%, in the cooling process previous to recording the spectrum it reaches 31%. Figure 3 shows two possible structures for the intermediate product after the loss of carboxylic groups. The theoretical values of weight loss corresponding to their formation are 34.9 and 33.2%, respectively.

The disappearance of the ν_{COOH} band is accompanied by the displacement of the $\nu_{\text{COO}}^{\text{as}}$ band from 1590 to 1640 cm^{-1} , which can be interpreted as a consequence of the greater covalent character of the Pd–O bonds [5]. The final position of the band is the same as that observed in the compound $[\text{Pd}(\text{PDТА-H}_2)] \cdot \text{H}_2\text{O}$ (1), in which there are two carboxylate groups bonded

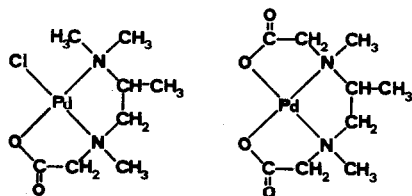


Fig. 3. Two possible structures for the intermediate product after the loss of carboxylic groups.

in the same way as that in the second structure proposed in Fig. 3. Further support for this structure is the appearance of carboxylate groups in the thermal decomposition of $[\text{Pd}(\text{PDTA-H}_4)\text{Cl}_2]$, a compound that did not possess these groups initially [6].

The following stage in the process of decomposition (up to 400°C) consists of the loss of carboxylate groups, proved by the disappearance of the corresponding band in the IR spectra. In the final stage combustion of the remaining organic material, leading to the formation of PdO occurs. The theoretical weight loss is 82%, which is the same as that obtained experimentally. To confirm formation of PdO, we studied the decomposition of the final product up to 900°C, observing an endothermic effect at 840°C and a weight loss of 16%, both corresponding to the decomposition of PdO with evolution of O₂ [7].

Decomposition of $[\text{Pd}(\text{PDTA-H}_3)\text{Br}] \cdot 2 \text{H}_2\text{O}$

The structural analogy between this compound and the preceding one led us to suppose that their thermal decomposition processes must be very similar. In fact, the only difference observed is in the shape of the exothermic effect associated with the combustion of the organic material, although the temperature range is the same for both complexes.

It is also interesting to note that the IR spectra of the intermediate products at 360 and 450°C show a weak band in the characteristic zone for C-H stretching, its intensity decreasing with increasing temperature. This fact supports the idea that the last stage in the decomposition is the pyrolysis and total combustion of the ethylenediamine backbone, as shown previously [2,3].

Decomposition of $[\text{Pd}_2(\text{CNS})_2(\text{PDTA-H}_2)] \cdot 2 \text{H}_2\text{O}$

The characterization of this complex [4] revealed great differences between it and other palladium complexes with PDTA, and we proposed a polymeric structure in which metallic ions are joined by thiocyanate and PDTA bridges. A comparison between the DTA and TG diagrams of Figs. 1 and 4 shows that these differences are also present in their thermal decomposition processes.

In the TG curve there is an initial weight loss of 5% corresponding to the release of the water of crystallization. (theoretical value 5.4%). The decomposition process continues at a temperature somewhat lower than in the halogenated complexes. In the IR spectrum of the intermediate at 190°C (Fig. 5), a displacement from 2160 to 2100 cm⁻¹ and a lower intensity are observed for the $\nu_{\text{SCN}}^{\text{as}}$ band, showing a change in the structural function of the thiocyanate groups. Figure 5 also shows that the loss of free carboxylic groups is completed in a narrower temperature range than in the other

complexes, and simultaneously to the breaking of the thiocyanate bridges. These facts suggest that after the breaking of the thiocyanate bridges, the coordination sites that become free are occupied by new carboxylate groups formed from free carboxylic groups.

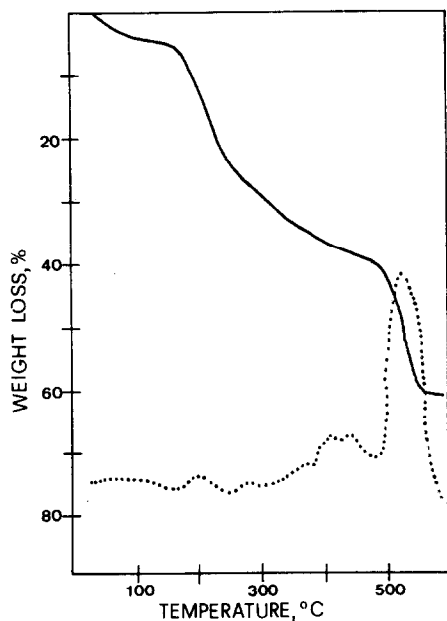


Fig. 4. DTA and TG curves for $[\text{Pd}_2(\text{CNS})_2(\text{PDTA-H}_2)] \cdot 2 \text{H}_2\text{O}$ in an atmosphere of static air.

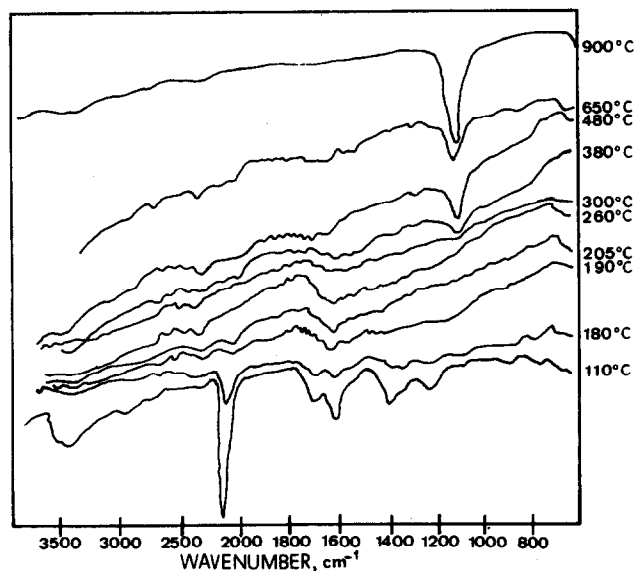


Fig. 5. IR spectra of some intermediate products in the decomposition of $[\text{Pd}_2(\text{CNS})_2(\text{PDTA-H}_2)] \cdot 2 \text{H}_2\text{O}$.

The endothermic effects at 250 and 300°C are associated with the loss of coordinated carboxylate groups and the release of thiocyanate groups, respectively, as is shown by the disappearance of the characteristic bands in the IR spectra (Fig. 5). The exothermic effects registered at ca. 400°C are associated with oxidation processes leading to the formation of sulfate ions, as shown by the appearance of an intense band at 1120 cm^{-1} [8] for all the intermediate products at temperatures higher than 380°C.

A sharp exothermic effect in DTA and a greater slope in the TG curve show that combustion of the remaining organic material occurs at temperatures higher than 500°C. It is interesting to note that the combustion temperature is greatly affected by the nature of the metallic ion and the presence of ligands other than PDTA.

The total weight loss (62%) is not the theoretical value for PdSO_4 formation, which means that other products must also be formed. The endothermic decomposition at 840°C shows the existence of PdO besides PdSO_4 , whose band still appears in the IR spectrum of the product heated to 900°C (Fig. 5). It seems that, after the breaking of the thiocyanate bridges, two independent decomposition processes occur. The first, starting at 380°C, is the decomposition of the remains with Pd-S bonds and leads to the formation of PdSO_4 ; the second is the decomposition of the fragments without Pd-S bonds and is similar to that observed for the halogenated complexes of palladium and PDTA, leading to PdO formation.

Decomposition of $[\text{Pd}_2(\text{PDTA-H}_3)_2(\text{en})]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$

This compound has a dimeric structure with tridentate PDTA, ethylenediamine acting as bridging group between two palladium ions [4]. The DTA and TG curves are very similar to those of the halogenated complexes. The loss of five molecules of water of crystallization occurs at the same temperature as in the other complexes and corresponds to a weight loss of 9% (theoretical value 8.6%).

In the IR spectra of the intermediate products between 190 and 215°C (Fig. 6), the $\nu_{\text{N-H}}^{\text{en}}$ bands lose intensity progressively and disappear, showing that in this temperature range ethylenediamine is lost. An endothermic effect in the DTA curve registered in an atmosphere of argon is associated with this stage, suggesting that the ethylenediamine is released without decomposition [8], although in an atmosphere of static air the molecule can be cracked after being released which can result in the appearance of an exothermic effect [9]. After this stage, the coordination sites that become free are occupied by chloride ions or carboxylate groups formed from carboxylic groups. The behavior observed for $[\text{Pd}(\text{PDTA-H}_4)\text{Cl}_2]$ [5] suggests the second possibility. Moreover, although in the IR spectrum of the intermediate product at 215°C a ν_{COOH} band is observed, the relative intensity of the bands appearing at 1700 and 1600 cm^{-1} shows a proportion of coordi-

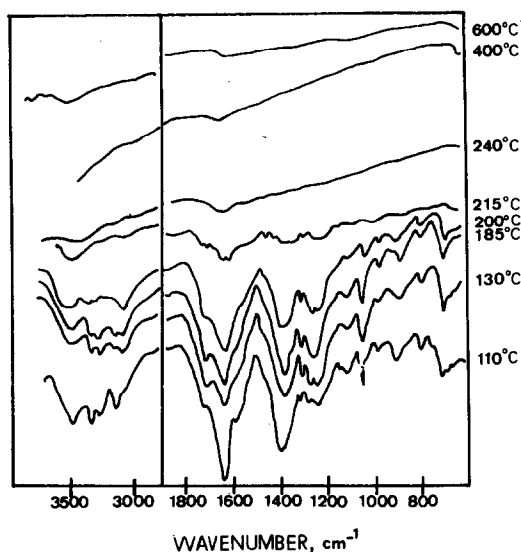


Fig. 6. IR spectra of some intermediate products in the decomposition of $[\text{Pd}_2(\text{PDTA-H}_3)\text{en}]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$.

nated carboxylate groups greater than in the initial compound.

The following stages in the thermal decomposition process are the same as those observed for the halogenated complexes of palladium and PDTA, leading to PdO formation. The total weight loss is 73% and the theoretical value is 76%.

CONCLUSION

The DTA and TG curves of the compounds studied in this paper are in agreement with those reported for other palladium complexes with PDTA [1]. The use of IR spectroscopy has led us to establish the sequence in which the several groups in the complex are released. This sequence is also in agreement with that obtained for PDTA and its sodium salts [3] by applying gas chromatography to the analysis of the gases evolved [2]. Nevertheless, it is interesting to note that the temperature at which the different steps of the decomposition occur are somewhat lower than those reported for free PDTA. The differences observed must be a consequence of the nature of the products, although they can be accentuated by the difference between the methods employed in both cases. Thus, when gas chromatography is applied, the temperature observed for the evolution of a product can be higher than that corresponding in the DTA-TG curves, because the gases may be delayed before reaching the chromatograph. In contrast, when IR spectroscopy is used, a displacement in the opposite direction is observed, as a

consequence of the weight loss occurring in the cooling process previous to recording the spectra. The extent to which this last effect occurs has been verified by heating and cooling the sample in successive cycles in which the maximum temperature is progressively increased. These diagrams demonstrate that there is an important weight loss in the cooling processes, showing that the conditions under which the experiments are carried out are far from those of thermodynamic equilibrium. Moreover, different weight losses are observed for every selected temperature, which shows that the decomposition process does not occur through well-defined steps. On the contrary, our results seem to indicate that this decomposition is a complex process in which several different overlapping reactions take place within rather similar temperature ranges.

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