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EGA/MS INVESTIGATIONS ON THE THERMAL DEGRADATION OF DIAMMONIUMHEXACHLOROPLATINATE

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Abstract

The thermal degradation of diammoniumhexachloroplatinate $(NH_4)_2PtCl_6$ is used in technical scale for the production of the pure platinum metal [1] and for this reason of great interest.

Our investigations have been focused on the influence of the different atmospheres (oxidizing, inert or reducing) used in the technical processes towards the degradation mechanism and the evolved volatile degradation products.

The second main aspect of our investigations was the evolution of volatile platinum species. Regarding the different frequencies of platinum allergies related to the different technical processes, the evolution of volatile platinum species is of great importance, due to the supposed allergic potential of this substances [2–4].

Keywords: degradation, evolved gas analysis, platinum, thermal analysis, thermogravimetry

Introduction

One of the earliest reports on the thermal degradation of diammoniumhexachloroplatinate was given by Wöhler [5], who translated a manuscript of Berzelius. In this report, the authors found the degradation products to be platinum, HCl, ammoniumchloride and water. In the literature [6], the degradation mechanism in inert atmosphere is given as

$$3(NH_4)_2PtCl_6 \xrightarrow{\Delta} 3Pt + 16HCl + 2NH_4Cl + 2N_2$$

Later, Ray and Gosh reported the formation of NH·HCl as well as inconsistencies within the quantification of the degradation products [7, 8].

A mechanism for the thermal degradation under reducing conditions (hydrogen atmosphere) was given by Pigeon [9]. He proposed the mechanism as

$$(NH_4)_2PtCl_6 \xrightarrow{+2H_2} Pt + 2NH_4Cl + 4HCl$$

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Experimental

Materials

The sample material of $(NH_4)_2PtCl_6$ was a product of the PRIOR Technologic GmbH with at least a 99.9% degree of purification.

Methods

The TG/DTG and EGA (MS) measurements were carried out using a STA 429 device (Netzsch) coupled with a QMS 420 Mass Spectrometer (Balzers) via a two-stage orifice system. For the investigations we used 25–30 mg of sample and 20 mg Al_2O_3 as inert reference material.

The investigations were carried out from ambient temperature up to ca 1000°C using a heating rate of 10 K min^{-1}. The simultaneously recorded mass spectra in the range of 1 to 100 amu were taken every 10 K, starting at 20°C using a scan rate of 20 ms/amu.

The investigations have been carried out under dynamic atmospheres with a flow of 140 mL min^{-1}. As reaction gases air, nitrogen and hydrogen have been used. The 'hydrogen' atmosphere was in fact a mixture of 10% hydrogen in nitrogen.

Additional special TG investigations, using a 50 mg sample were carried out for the detection of evolved platinum species. For this investigations we used a STA 409 (Netzsch) coupled with a QMS 421 (Balzers) Mass Spectrometer via a Simmer® – Interface.

Since no information about the platinum radical species was available, the mass spectrometric investigations were done in the so-called MID (Multiple Ion Detection) mode. The three platinum isotopes (^{194}Pt, ^{195}Pt and ^{196}Pt) with the highest natural abundance were scanned continuously, using a sampling time of 0.2 s.

Results and discussion

Air atmosphere

The degradation of the platinum complex occurs in the temperature range of 300 to 450°C in one step with a maximum at 404°C (DTG T_p). This degradation step does not show any significant thermal effect indicated by the DTA. The experimental mass loss of 55.61% is in good agreement with the theoretical value (56.05%) (Fig. 1).

The degradation results under cleaving of NH_3 and HCl. A formation of Cl_2 could not be detected. Due to these results, it can be assumed, that a part of the NH_3 is oxidized on the one hand by the oxygen of the surrounding atmosphere and on the other hand by Cl radicals, formed during the degradation process. The courses of the evolution of water (*m/z* 18), ammonia (*m/z* 17) as well as hydrogen-chloride (*m/z* 35, 36, 37 and 38) are given in Figs 2 and 3.

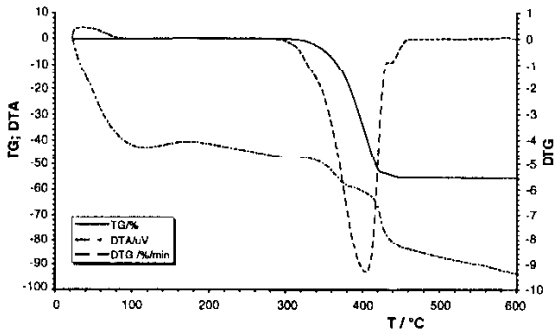

Fig. 1 TG, DTG and DTA curves of the thermal degradation of $(NH_4)_2PtCl_6$ in air

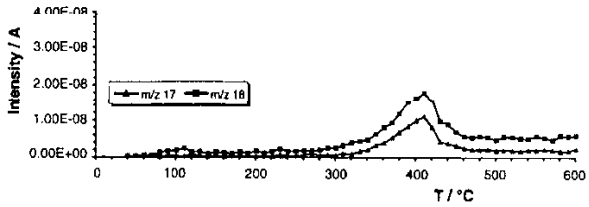

Fig. 2 Evolution of water (*m/z* 18) and NH_3 (*m/z* 17) during the thermal degradation of $(NH_4)_2PtCl_6$ in air

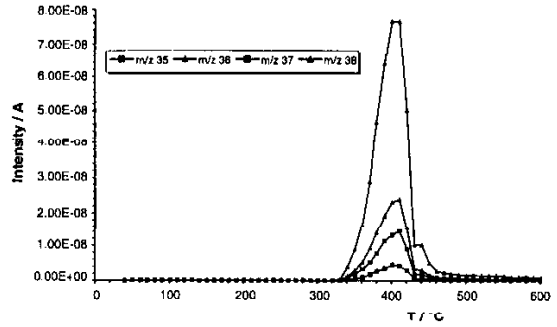

Fig. 3 Evolution of HCl during the thermal degradation of $(NH_4)_2PtCl_6$ in air

Nitrogen atmosphere

The degradation of the Pt-complex in a nitrogen atmosphere is the same as under air atmosphere, except the formation of water due to the oxidation of NH_3 by the atmospheric oxygen. As it can be seen from Figs 4 and 5. Also NH_3 and HCl are evolved during the degradation process. Again no Cl_2 could be detected.

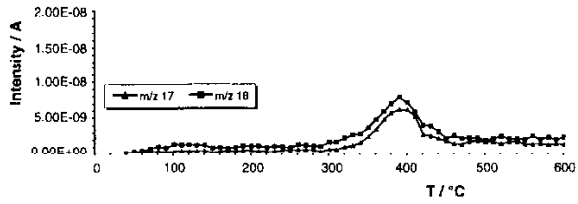

Fig. 4 Evolution of water (*m/z* 18) and NH_3 (*m/z* 17) during the thermal degradation of $(NH_4)_2PtCl_6$ in a nitrogen atmosphere

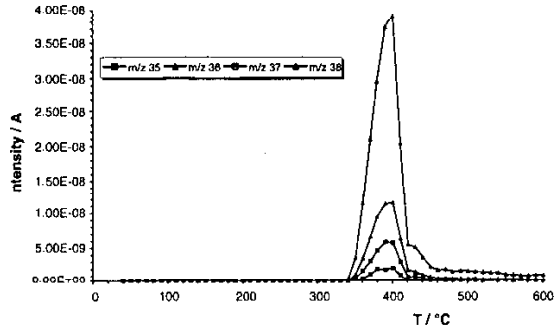

Fig. 5 Evolution of HCl during the thermal degradation of $(NH_4)_2PtCl_6$ in a nitrogen atmosphere

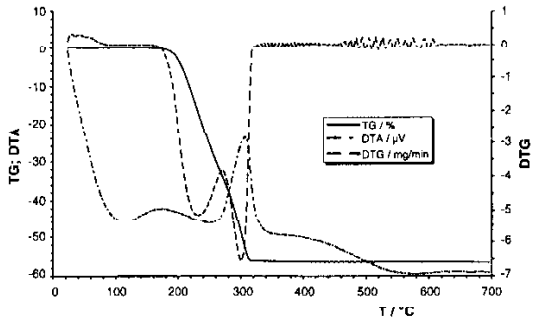

Fig. 6 TG, DTG and DTA curves of the thermal degradation of $(NH_4)_2PtCl_6$ in a hydrogen atmosphere

Hydrogen atmosphere

The investigation of the complex under reductive conditions is complete different to the degradation under air or nitrogen atmosphere. The thermal analysis curves (TG and DTG as well as the DTA) clearly indicate a two-step degradation mecha-

nism. Under these conditions, the complex will be decomposed in the first step under formation of HCl to the platinum metal and ammoniumchloride. The second step is related to the sublimation of NH_4Cl. The experimental values of the mass losses during the single steps are in good agreement with the theoretical values. The thermal analysis curves are given in Fig. 6 and the values are listed in Table 1.

Table 1 Data of the thermal degradation of $(NH_4)_2PtCl_6$ in a hydrogen atmosphere

Step	TG $\Delta m/\%$	DTG $T_p/^oC$	DTA $T_p/^oC$
1	–34.71	233	
2	–21.56	300	307 endo
sum	56.27		
residue	43.53		

The interpretation of the on-line archived mass spectra also lead to this result. During the first degradation step only HCl was detected, while in the second degradation step NH_3 was found beneath HCl (Figs 7 and 8).

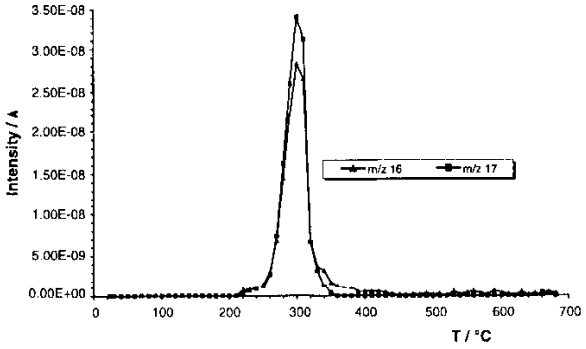

Fig. 7 Evolution of NH_3 during the thermal degradation of $(NH_4)_2PtCl_6$ in a hydrogen atmosphere

Evolution of platinum-species

For the investigation of the sample with respect to the evolution of platinum-species, the sample have been investigated using the so-called MID modus within the mass spectrometric detection. Since no information about the platinum species were available, the three platinum isotopes with the highest natural abundance were scanned continuously in a high sensitive mode.

As it can be seen from the ion current intensity curves for the platinum isotopes in Figs 9–11 platinum was clearly detected in the gas phase in nitrogen atmosphere (Fig. 10). A narrow peak with its maximum at 360°C indicates a relative high

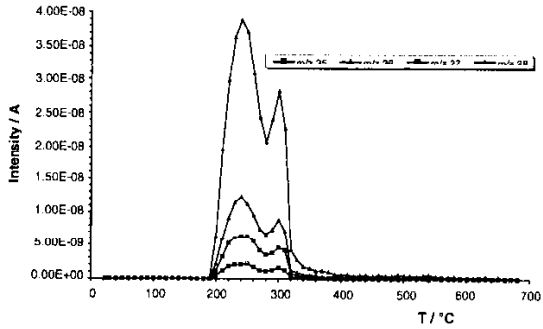

Fig. 8 Evolution of HCl during the thermal degradation of $(NH_4)_2PtCl_6$ in a hydrogen atmosphere

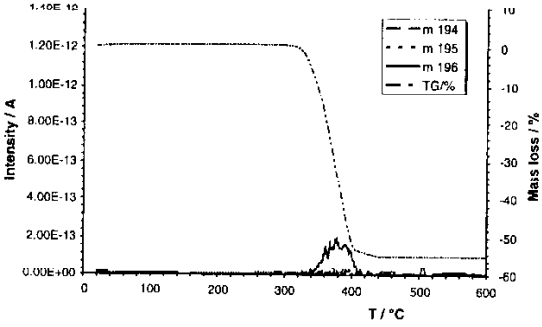

Fig. 9 TG curve and evolution of platinum species during the thermal degradation of $(NH_4)_2PtCl_6$ in air

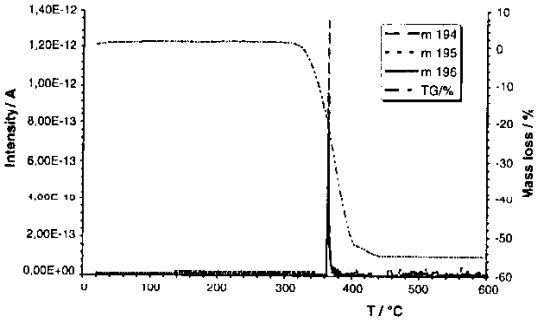

Fig. 10 TG curve and evolution of platinum species during the thermal degradation of $(NH_4)_2PtCl_6$ in a nitrogen atmosphere

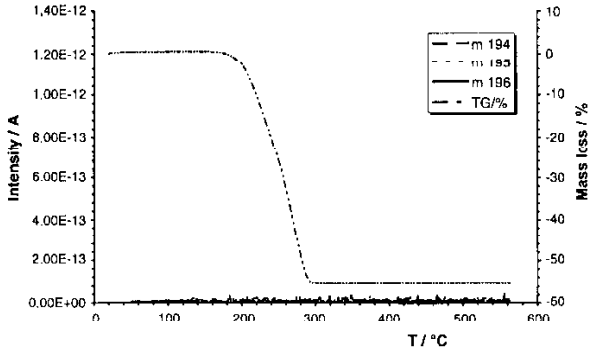

Fig. 11 TG curve and evolution of platinum species during the thermal degradation of $(NH_4)_2PtCl_6$ in a hydrogen atmosphere

amount of platinum compared to the degradation under air atmosphere. Under air atmosphere, a relative broad peak, starting at 320 and ending at 420°C was observed (Fig. 9).

The reducing conditions in hydrogen atmosphere seem to avoid the evolution of platinum species. Due to the different degradation mechanism, no Pt isotopes were detected.

Conclusions

The main degradation processes of the thermal decomposition of $(NH_4)_2PtCl_6$ follow the mechanisms given in the literature. Nevertheless, in inert or oxidising atmosphere, there is a minor degradation pathway leading to the evolution of volatile platinum species. Further work has to be done with respect to this special pathway.

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