

The Differences in Thermal Breakdown of H_2PtCl_6 and *cis*- $Pt(NH_3)_2Cl_2$ in Carbon Furnace Atomic Absorption.

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ABSTRAK

Kajian menggunakan analisis termogravimetri dan penyerakan x-ray menunjukkan larutan asid heksakloroplatinik (H_2PtCl_6), yang selalu digunakan sebagai larutan piawai di dalam teknik spektrofotometri serapan atom (AAS), diubah kepada $PtCl_2$ yang mudah meruap sebelum menjadi logam platinum. Sebaliknya larutan *cis*-diaminodikloroplatinum (II) (*Cis*- $Pt(NH_3)_2Cl_2$; *cis*-DDP) diubah terus kepada logam platinum. Perbezaan mekanisma penguraian oleh haba ini mungkin menjadi salah satu daripada sebab mengapa isyarat spektrofotometri serapan atom relau karbon (CFAAS) bagi H_2PtCl_6 lebih rendah daripada *cis*-DDP.

ABSTRACT

A study using a combination of thermogravimetric and x-ray diffraction analyses has shown that a solution of hexachloroplatinic acid (H_2PtCl_6), usually used as a standard in atomic absorption spectrophotometric (AAS) measurements, was broken down to yield volatile $PtCl_2$ before being converted to metallic platinum. On the other hand, a solution of *cis*-diaminodichloroplatinum(II) (*cis*- $Pt(NH_3)_2Cl_2$; *cis*-DDP) was converted to metallic platinum in a single step. The differences in their thermal decomposition mechanisms could be one of the reasons as to why carbon furnace atomic absorption spectrophotometric (CFAAS) signal from H_2PtCl_6 was found to be lower than that of *cis*-DDP in aqueous solution.

INTRODUCTION

Studies by earlier workers have shown differences in absorbance signals of platinum from different platinum complexes when analysed by flame AAS technique. For example, the platinum absorbance of $(NH_4)_2PtCl_4$ (50 ppm) is about twofold greater than that of K_2PtCl_6 (Macquet and Theophanides 1974) and the *cis*-DDP signal is about 12% higher than that of H_2PtCl_6 (Macquet *et al.* 1974). These differences are said to be due to the differences in thermal stability of the complexes. The ability of the more stable complex to survive as volatile species in the flame is greater than the less stable complexes; a volatile species is more easily decomposed to free atoms hence a higher AAS signal is obtained. (Macquet and Theophanides

1975). The same explanation was also given for the depression of platinum signals from H_2PtCl_6 in the flame by several anions and cations.

H_2PtCl_6 is a compound which is formed when Pt metal is dissolved in aqua regia and diluted in hydrochloric acid after the evaporation of nitric acid. The solution is used as standard for platinum analysis using AAS techniques because it is available commercially or can be easily prepared.

In our preliminary attempt to analyse Pt in serum and urine from patients who were being treated with *cis*-DDP, using CFAAS, it was found that the recovery of analysis was always high (129-165%) (Haron, M.J. 1982). The analysis and the recovery was done using H_2PtCl_6 as standard. It was also found that at a

concentration of 500 ppb Pt in 0.05M HCl, the absorbance peak height signal of cis-DDP was higher by 38% compared to H_2PtCl_6 .

This article describes the differences in mechanism of the thermal breakdown between H_2PtCl_6 and cis-DDP solutions that possibly occur in a carbon furnace atomic absorption during the atomization process. This work was carried out as part of the effort to optimize the CFAAS technique for the analysis of platinum in biological fluid i.e. serum, urine and cerebral fluid from patients after treatment with the drug cis-DDP for various types of cancer (Rozenzweig *et al.* 1977).

MATERIALS AND METHODS

Stock standard containing 1000 ppm Pt as H_2PtCl_6 in 1M HCl was obtained from BDH Chemicals Ltd. Cis-DDP salt was obtained from Mead-Johnson Ltd and an appropriate amount was dissolved in 1M HCl to give the 1000 ppm Pt solution used as stock standard.

The curve for thermal breakdown of the compounds from the solutions were recorded using a Stanton Redcroft TG 750 thermobalance which consists of a microfurnace and electronic balance, and a two-pen Speedomax strip-chart recorder.

A platinum crucible (40 ml), which was supplied by the manufacturers, was tared on the microbalance at an argon flow rate of 20 ml min^{-1} . A sample solution (30 μ l) containing about 3 mg of platinum as H_2PtCl_6 or cis-DDP was transferred into the crucible using an Eppendorf micropipette. The solutions were prepared by evaporation of 100 ml solution of 1000 ppm platinum in 1M HCl to 1 ml; the evaporation was accomplished at a temperature between 90-100°C. The thermogravimetric curve was recorded as the sample was heated at a heating rate of 30°C min^{-1} from ambient temperature to the maximum available temperature of 1000°C.

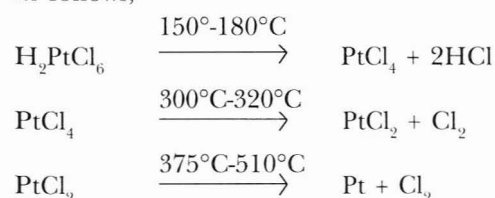
A Philips x-ray generator equipped with a Debye-Scherrer camera was used to record the x-ray diffraction patterns of the residues formed by heating the H_2PtCl_6 solutions to about 350°C in the thermobalance or in carbon furnace using HGA 500 Perkin Elmer graphite atomiser.

The preparation of samples in the carbon furnace for the x-ray analysis was done as fol-

lows: A stock solution of H_2PtCl_6 (10 μ l) was injected into the furnace and the solution was dried at 100°C for 20 seconds with 20 seconds ramp time. The temperature was increased to 350°C for 40 seconds with 40 seconds ramp time. After cooling, the procedure was repeated three times to obtain enough sample. The residue was scraped from the furnace using a stainless steel spatula and analysed by x-ray method.

RESULTS AND DISCUSSION

Figure 1 shows a trace of the thermal breakdown curve of H_2PtCl_6 as recorded by the thermobalance. The pattern was similar to previously reported data (Rowston and Ottaway 1979). Schweizer and Kerr (1978) found that the thermal breakdown of H_2PtCl_6 , H_2O salt to form platinum metal occurred through several steps as follows;



Plateaus A, B, C and D (*Figure 1*) correspond to H_2PtCl_6 , $PtCl_4$, $PtCl_2$ and platinum metal respectively. In order to confirm the existence of $PtCl_2$, the residue from a thermogram on heating the solution to the plateau C and from carbon furnace on heating the solution to 350°C was analysed by x-ray powder diffraction, following the method published by Rowston and Ottaway (1979). The d spacings of the x-ray pattern were calculated and compared with the standard values for $PtCl_2$ (The Powder Diffraction File 1972). The results showed that the residue from the thermobalance at plateau C and the carbon furnace contained only $PtCl_2$. A typical example of the x-ray pattern of the residue from carbon furnace is shown in Table 1.

$PtCl_2$ is known to have different crystal-line forms, α and β (Wiese *et al.* 1970). The latter, which is formed in this process (Schweizer and Kerr 1978), contains discrete Pt_6Cl_{12} units and is volatile (Schafer *et al.* 1967); Landsberg and Schaller, 1971). From the thermogravimetric traces, the number of moles of platinum

metal and $PtCl_2$ were calculated. It was found that 12% (mean) of the platinum is lost during the breakdown of $PtCl_2$ to Pt metal (Haron 1982). However the amount of platinum lost during the conversion varies with sample size, heating rate and flow rate of the inert gas used (Schweizer and Kerr 1978).

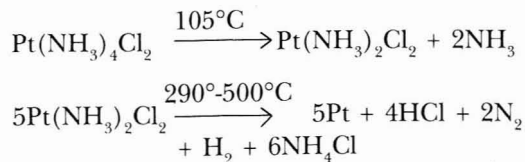
TABLE 1

X-ray powder diffraction analysis of residue obtained after heating 30 ul aqueous solution of H_2PtCl_6 (0.3 mg Pt) in carbon furnace AAS to $350^\circ C$. X-ray conditions : source Cu K (1.54 nm) radiation

Lattice parameters (nm)	
Calculated	Literature*($PtCl_2$)
0.673	0.669
0.400	0.403
0.374	0.378
0.323	0.325
0.292	0.293
0.265	0.268
0.227	0.228
0.199	0.200
0.187	0.187
0.176	0.177
0.164	0.163

* The Powder Diffraction File, (1972).

On the other hand, the trace of thermal breakdown curve of cis-DDP solution shows that the compound is converted to metallic platinum in the temperature range $290-500^\circ C$ in a single step (Figure 2). This is similar to the thermogravimetric data on $Pt(NH_3)_4Cl_2$ reported earlier by Kerr and Chester (1971). They have shown that DDP, which was formed as an intermediate during the thermal breakdown of $Pt(NH_3)_4Cl_2$, was converted to platinum metal in a single step, as shown below:



From the thermogravimetric traces (Figure 2) it can be seen that cis-DDP was converted to metallic platinum without any significant loss.

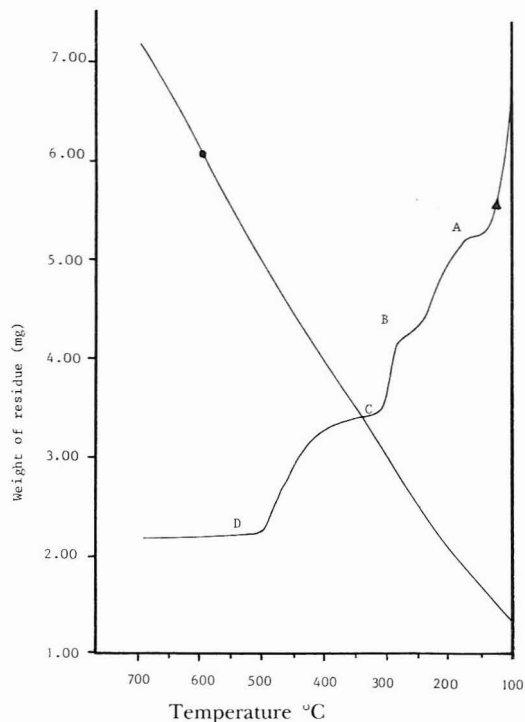


Fig. 1. Thermogravimetric curve (▲) for a solution of H_2PtCl_6 in hydrochloric acid. The residue on the plateau were H_2PtCl_6 (A), $PtCl_4$ (B), $PtCl_2$ (C) and Pt metal (D). The line (•) is a temperature calibration.

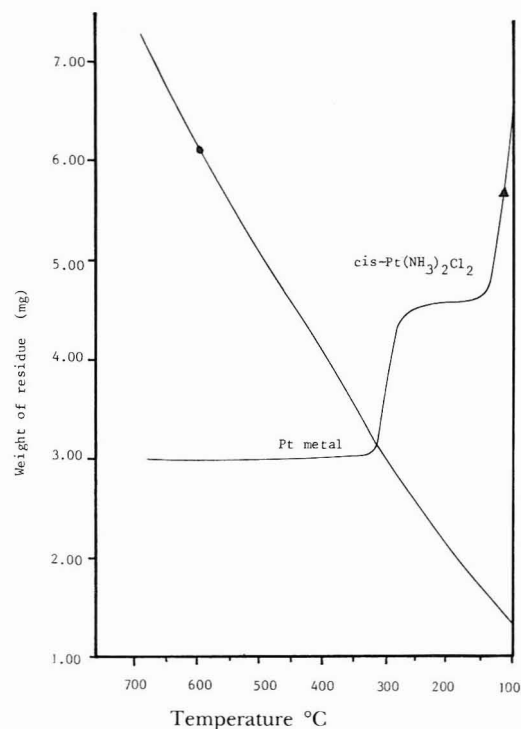


Fig. 2. Thermogravimetric curve (▲) for cis- $Pt(NH_3)_2Cl_2$ in a hydrochloric acid solution. The line (•) is a temperature calibration.

CONCLUSION

In a carbon furnace, cis-DDP could also be converted to metallic platinum in a single step, whereas H_2PtCl_6 was shown to be converted to $PtCl_2$ before being converted to metallic platinum. The $PtCl_2$ formed, which is volatile, could be swept out by the flow of the argon gas (used to protect the carbon furnace) in the same manner as in the thermobalance. This could be the explanation for the lower platinum signals given by H_2PtCl_6 compared to those by cis-DDP in CFAAS. It is therefore suggested here that cis-DDP be used as a standard for analysis of biological samples containing cis-DDP.

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