

THERMAL STABILITY OF SOME PLATINUM COMPLEXES

JOSÉ O. HERNÁNDEZ and EDUARDO A. CHOREN

Laboratorio de Superficies, Escuela de Ingeniería Química, Facultad de Ingeniería, Universidad del Zulia, Apartado 526, Maracaibo (Venezuela)

(Received 27 June 1983)

ABSTRACT

The thermal decomposition of some platinum(II) and platinum(IV) complexes was studied using thermogravimetric and differential thermal analysis (TG and DTA) techniques. The platinum complexes studied were: dihydrogen hexachloroplatinate(IV) ($\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$); ammonium tetrachloroplatinate(II) $[(\text{NH}_4)_2\text{PtCl}_4]$; diammineplatinum(II) nitrite $[(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2]$; tetraammineplatinum(II) nitrate $[\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2]$ and tetraammineplatinum(II) chloride $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}]$.

Thermal analysis was carried out under an atmosphere of helium, hydrogen or oxygen (60 ml min^{-1}). Generally, a lower thermal stability under hydrogen atmosphere than helium or oxygen atmospheres was observed. Endothermic decomposition of chlorine complexes and exothermic decomposition of nitrite and nitrate complexes were also observed.

INTRODUCTION

Platinum complexes are widely used for the manufacture of industrial catalysts. These catalysts are prepared by impregnation of a support (usually alumina) with a solution of the complex, dried and thermally treated in order to obtain a high metal dispersion on the surface. In studies involving catalysts it is very important to know the thermal behavior of platinum complexes under different atmospheres in order to interpret the decomposition path of these complexes on the support surface.

Platinum complexes are usually present with a planar or octahedral geometry [1]. Their transformation can be:

- ligand isomerization [2] (generally exothermic);
- ligand exchange or substitution;
- ligand elimination [3] (generally endothermic);
- decomposition (endothermic or exothermic) [4].

In this work the influence of different atmospheres on the thermal transformation of some platinum complexes is studied.

EXPERIMENTAL

Materials

The platinum complexes studied were dihydrogen hexachloroplatinate(IV) ($\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$), ammonium tetrachloroplatinate(II) $[(\text{NH}_4)_2\text{PtCl}_4]$, diammineplatinum(II) nitrite $[(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2]$, tetraammineplatinum(II) nitrate $[\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2]$ and tetraammineplatinum(II) chloride $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}]$; all the analytical reagents were from Alfa Div., Ventron Corp., and were used without further purification.

Helium, hydrogen and oxygen ultra-high purity gases (UHP) were from Linde Div., Union Carbide.

Equipment

A DuPont 900 thermal analyzer with a DTA and TGA device was used. DTA and TG were carried out under a gas flow (60 ml min^{-1}) of oxygen.

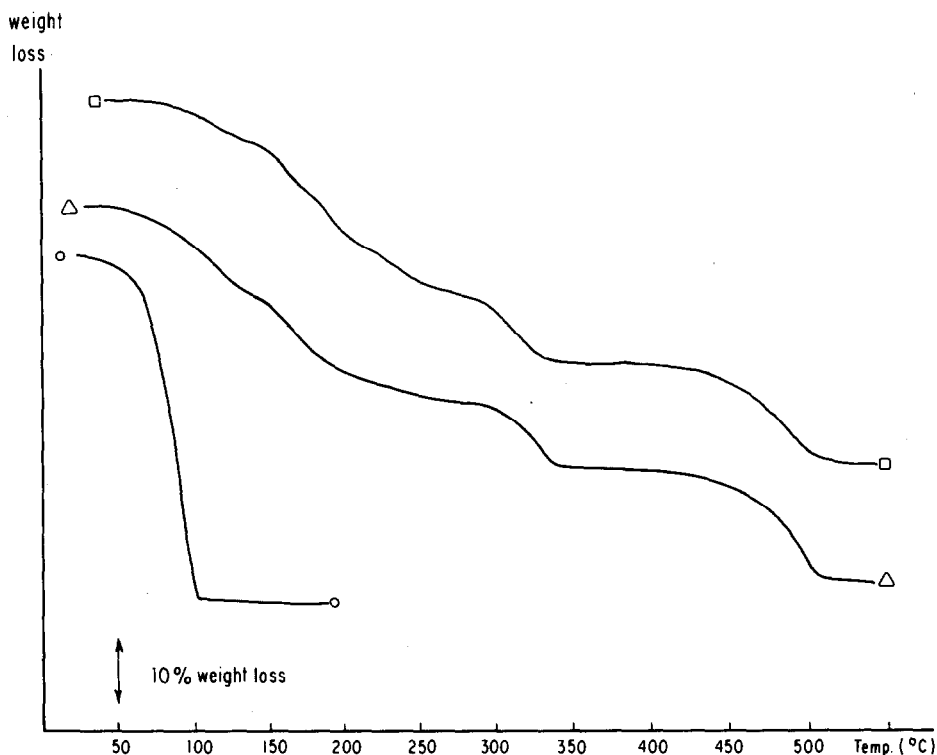


Fig. 1. TG of dihydrogen hexachloroplatinate(IV), $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$. Temperature program 10 K min^{-1} ; $P = 1 \text{ atm}$. ○, Hydrogen (60 ml min^{-1}); □, helium (60 ml min^{-1}); and Δ, oxygen (60 ml min^{-1}).

hydrogen or helium. The temperature program was 10 K min^{-1} for all the experiments. Platinum sample and reference holders were used. The reference material for DTA was alumina.

RESULTS

Typical TG and DTA diagrams for dihydrogen hexachloroplatinate(IV) and ammonium tetrachloroplatinate(II) are shown in Figs. 1–4. Thermal decomposition results are summarized in Table 1.

The diagrams for all the complexes under an atmosphere of oxygen or helium are similar. These results show that no platinum oxides are formed during the decomposition of the complexes to platinum metal.

TABLE 1

Thermal stability of some platinum complexes in different atmospheres

Complex	Atmosphere ^a	Transformation temp. (°C)	Thermal nature of the transformation	Products of the transformation ^b
$\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$	Oxygen	50–200	Endothermic	H_2O , HCl , PtCl_4
		320–330	Endothermic	Cl_2 , PtCl_2
		480–490	Endothermic	Cl_2 , Pt
	Helium	75–280	Endothermic	H_2O , HCl , PtCl_4
		320–330	Endothermic	Cl_2 , PtCl_2
		480–490	Endothermic	Cl_2 , Pt
Hydrogen	30–90	Endothermic	Pt	
	Oxygen	290	Slightly endothermic	NH_4Cl , NH_4PtCl_3
		335	Endothermic	Cl_2 , NH_4Cl , Pt
$(\text{NH}_4)_2\text{PtCl}_4$	Helium	270	Slightly endothermic	NH_4Cl , NH_4PtCl_3
		330	Endothermic	Cl_2 , NH_4Cl , Pt
	Hydrogen	175	Slightly endothermic	HCl , $(\text{NH}_3)_2\text{PtCl}_2$
		245	Endothermic	NH_4Cl , Pt
$(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2$	Oxygen	240	Highly exothermic	Pt
	Helium	240	Highly exothermic	Pt
	Hydrogen	125	Highly exothermic	Pt
$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	Helium	260	Highly exothermic	Pt
	Hydrogen	190	Highly exothermic	Pt
$\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$	Helium	250	Endothermic	
		330	Endothermic	
		70	Endothermic	
	Hydrogen	260	Endothermic	

^a Gas flow 60 ml min^{-1} .

^b Calculated according to TG diagrams.

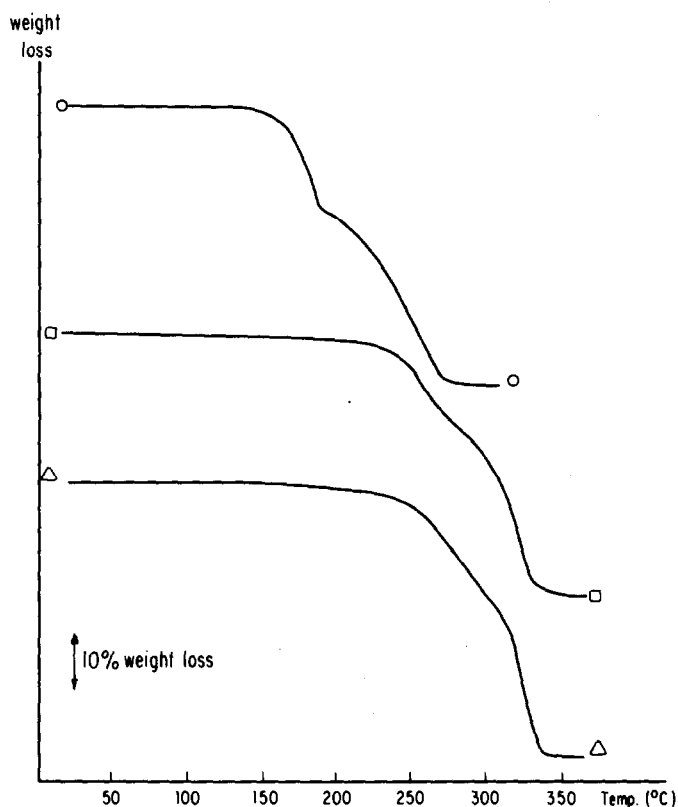


Fig. 2. TG of ammonium tetrachloroplatinate(II), $(\text{NH}_4)_2\text{PtCl}_4$. Temperature program 10 K min^{-1} ; $P = 1 \text{ atm}$. ○, Hydrogen (60 ml min^{-1}); □, helium (60 ml min^{-1}); and △, oxygen (60 ml min^{-1}).

DISCUSSION

The decomposition paths of the inorganic platinum complexes studied, which finally produce platinum metal, are strongly influenced by the nature of the complex and the atmosphere present.

In the case of dihydrogen hexachloroplatinate(IV) in an atmosphere of helium, it is observed that between room temperature and 150°C there is a loss of water and probably some chlorohydric acid. At 150°C the total decomposition into PtCl_4 [1] accelerates and finishes at 300°C . At 320°C the decomposition of PtCl_4 starts to form a plateau between 375 – 400°C , corresponding to platinum dichloride (PtCl_2), which decomposes between 400 and 500°C , finally giving platinum metal. The decomposition path is similar under a flow of oxygen, indicating that the oxidant atmosphere does not modify the mechanism of the decomposition.

In an atmosphere of hydrogen dihydrogen hexachloroplatinate(IV) de-

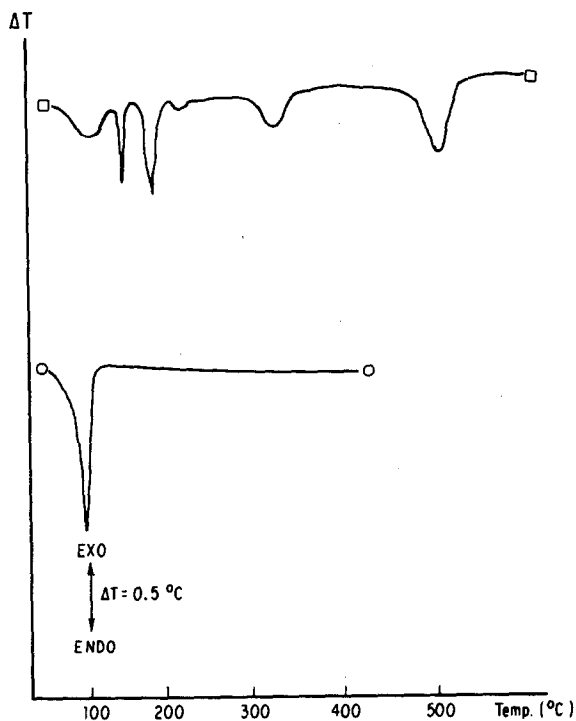


Fig. 3. DTA of dihydrogen hexachloroplatinate(IV), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Temperature program 10 K min^{-1} ; $P = 1\text{ atm}$. Reference material = α -alumina. \circ , Hydrogen (60 ml min^{-1}); and \square , helium (60 ml min^{-1}).

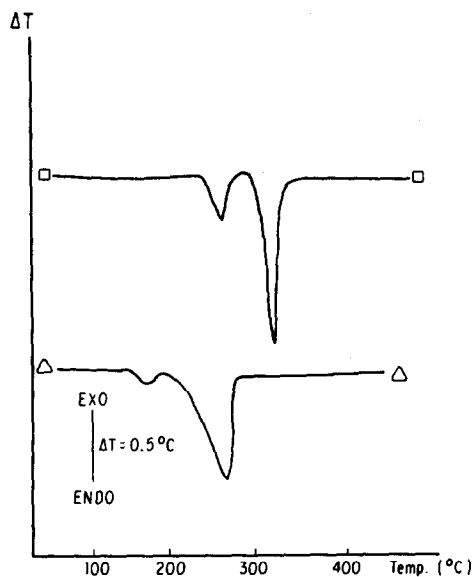


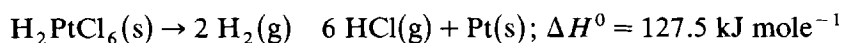
Fig. 4. DTA of ammonium tetrachloroplatinate(II), $(\text{NH}_4)_2\text{PtCl}_4$. Temperature program 10 K min^{-1} ; $P = 1\text{ atm}$. Reference material = α -alumina. \triangle , Hydrogen (60 ml min^{-1}); and \square , helium (60 ml min^{-1}).

composes totally between 50 and 100°C. This can be explained considering the enthalpy of decomposition of the complex under the different atmospheres. Using as reference the normal enthalpies of formation at 25°C, [5] we obtained:

<i>Helium atmosphere</i>	$\Delta H^0(\text{kJ mole}^{-1})$
$\text{H}_2\text{PtCl}_6(\text{s}) \rightarrow 2 \text{HCl}(\text{g}) + \text{PtCl}_4(\text{s})$	233.7
$\text{PtCl}_4(\text{s}) \rightarrow \text{Cl}_2(\text{g}) + \text{PtCl}_2(\text{s})$	114.5
$\text{PtCl}_2(\text{s}) \rightarrow \text{Cl}_2(\text{g}) + \text{Pt}(\text{s})$	148.4
$\text{H}_2\text{PtCl}_6(\text{s}) \rightarrow 2 \text{HCl}(\text{g}) + 2 \text{Cl}_2(\text{g}) + \text{Pt}(\text{s})$	496.6

The decomposition reaction is highly endothermic.

Hydrogen atmosphere



The enthalpy change is four times smaller. This analysis indicates that the decomposition must occur at a lower temperature, this fact was experimentally observed. It was also observed from the TG diagram that the decomposition is faster under hydrogen than under helium or oxygen flow.

The ammonium tetrachloroplatinate(II) $[(\text{NH}_4)_2\text{PtCl}_4]$, under helium atmosphere, decomposes at a temperature lower than 350°C, forming platinum metal. TG diagrams show two peaks in the differential weight-loss curve, the second peak mounted over the tail of the first peak, which makes identification of the intermediate product of decomposition difficult. However, an inflection point is observed at 275°C corresponding to a weight loss of 15%, suggesting the following reaction sequence

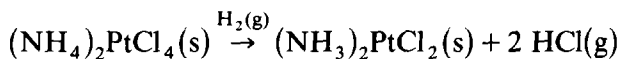


This explanation is strengthened by the low temperature of decomposition to platinum metal. If the resultant compound of the first stage of the decomposition were PtCl_2 , the decomposition would not begin before 350°C, which was found studying the H_2PtCl_6 thermal behavior. Further evidence for the reaction path suggested is the detection in the first stage of chloride ion using silver nitrate as indicator.

The decomposition of ammonium tetrachloroplatinate(II) under oxygen flow occurs in a similar way.

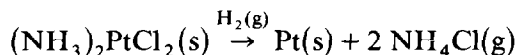
The thermal behavior of ammonium tetrachloroplatinate(II) is different to that discussed previously under hydrogen flow. Analysis of the TG and DTA diagrams shows that this complex is less stable in this atmosphere and its decomposition occurs in two stages. In the first stage the reaction path shows a maximum at 175°C with a weight loss of 20%. This transformation would correspond with the formation of the diammine platinum(II) chloride $[(\text{NH}_3)_2\text{PtCl}_2]$ complex by ligand exchange and elimination according to the

reaction



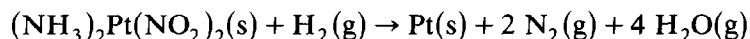
This compound was synthesized forming *cis* and *trans* isomers [1]. Also in accordance with the DTA diagram, it is observed that this transformation is slightly endothermic, which is in agreement with the ligand exchange in the coordinator sphere of the complex.

The second stage of the transformation corresponds to ligand elimination by the reaction



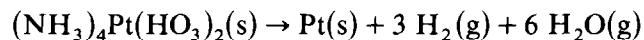
This reaction is endothermic involving a higher energy consumption than the first transformation. Similar results have been reported by Kukushkin et al. [2,3] for Pt(II) complexes.

The thermal behavior of diammine platinum(II) nitrite differs with the thermal behavior of the complexes discussed previously. Indeed, under the different atmospheres used this complex decomposes exothermically and rapidly. The decomposition temperature is lower in hydrogen (125°C) and probably occurs according to the reaction



Under helium or oxygen, decomposition occurs exothermically at 240°C in a single step.

The tetraammine platinum(II) nitrate decomposes exothermically in hydrogen or helium. In helium, decomposition takes place totally and violently at 260°C according to the reaction



In hydrogen, decomposition takes place at 190°C.

Tetraammine platinum(II) chloride presents a DTA diagram with two endothermic peaks in helium or hydrogen: at 250 and 330°C in helium and at 70 and 260°C in hydrogen, indicating that thermal stability of this complex, as in the complexes studied previously, is considerably lower in a reducing atmosphere, giving platinum metal at low temperatures.

ACKNOWLEDGEMENTS

The authors are indebted to Prof. Carlos Vinante, from Universidad del Zulia, Dr. Ignacio Rodon and Dr. Mario Urdaneta from INDESCA C.A. for many helpful discussions.

This work was partially supported by CONICIT (Venezuela) through Project S11-198.

REFERENCES

- 1 F. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 3rd edn., 1972, p. 1031.
- 2 Yu.H. Kukushkin and S.I. Bakhireva, *Russ. J. Inorg. Chem.*, 21(10) (1976) 1497.
- 3 Yu.H. Kukushkin, Y.P. Kotelnikov and V.M. Spevak. *Russ. J. Inorg. Chem.*, 22(8) (1977) 1194.
- 4 S.J. Ashcroft and C.T. Motimer, *Thermochemistry of Transition Metal Complexes*, Academic Press, London, 1970, p. 372.
- 5 C.R.C. *Handbook of Chemistry and Physics*, CRC Press, Inc., 56th edn., 1975-1976, p. D45.