

## KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA XXVII. Thermal decomposition of some metal and ammonium salts of hexachloroplatinic acid

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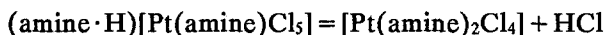
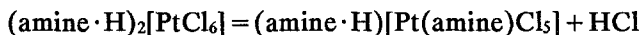
Nineteen salts of hexachloroplatinic acid with monovalent metals, aromatic and heterocyclic amines and phosphine were obtained and characterized by chemical analysis. The thermal decomposition of these complexes was studied by means of derivatograph and differential scanning calorimetry. The nature of the pyrolysis processes is discussed. From the TG curves, kinetic parameters were derived for different stages of the thermal decompositions.

### Introduction

Hexachloroplatinic acid,  $H_2[PtCl_6]$ , a dibasic complex acid, forms well-defined neutral salts with the alkali metals, with the monovalent transition metals (Ag, Tl), and with metal(III)-amine complex cations of the monoacidopentamine and diacidotetramine types ( $M = Co, Cr, Rh, Ir$ ). These latter salts are very sparingly soluble in water and can be used for the characterization of the corresponding complex cations [1–3]. The very sparingly soluble derivatives of the heavier alkali metals are also of some analytical importance.

The ammonium salts of the  $(amine \cdot H)_2[PtCl_6]$  type can be isolated from acidic media. These derivatives are well-defined, characteristic crystalline products, which can be recrystallized from dilute HCl solution. A series of ammonium salts with aliphatic mono- and diamines [4–7], aromatic amines

[8], N-heterocyclic bases [9], phosphines [10] and arsines [11] have been isolated and characterized. They decompose on boiling in aqueous solution and especially in the presence of NaOH. The boiling of aqueous solutions of the hexachloroplatinates of some heterocyclic N-bases leads to the formation of tetraacidodiamines:



In some cases the pentaacidomonoamine intermediate can be isolated too [12–13]. These processes are sometimes accompanied by redox phenomena: Pt(IV) → Pt(II).

Some thermal properties of the ammonium salts were also studied. The melting temperature of these substances are given in the majority of the cases. It was observed that before melting a dark resinous mass is formed. In some cases the melting process cannot be characterized by a well-defined melting point and is accompanied by partial decomposition. Quantitative measurements on the thermal decomposition of the hexachloroplatinates were made manometrically in chlorine atmosphere in the case of the free acid and the alkali metal salts [14–16].

In the present paper, 19 salts of  $\text{H}_2[\text{PtCl}_6]$  were obtained and studied by derivatograph and by differential scanning calorimetry.

## Results and discussion

The complex salts obtained by double exchange reactions in neutral solution (metal salts) and in acidic media (ammonium salts) are characterized in Table 1.

The thermal decompositions of the complexes studied depend very much on the nature of the outer sphere cation and generally occur in several successive stages. The final product is always metallic platinum. The pyrolysis is the simplest in the cases of complexes 1–4. As an example, the TG curves of the K and  $\text{NH}_4$  salts are given in Fig. 1.

It is seen that the K salt decomposes in two stages. The first stage involves the following reaction:

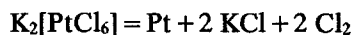


Table 1 M<sub>2</sub>[PtCl<sub>6</sub>] and (amine · H)<sub>2</sub>[PtCl<sub>6</sub>] · n H<sub>2</sub>O salts obtained

No.	Complex	Mol.wt. calcd.	Appearance	Analysis, %	
				Calcd.	Found
1.	K <sub>2</sub> · A	486.2	yellow octahedral cryst.	Pt 40.15	40.29
2.	Cs <sub>2</sub> · A	674	yellow microcryst.	Pt 28.96	28.70
3.	Tl <sub>2</sub> · A	817	thin yellow prisms	Pt 23.89	23.60
4.	(NH <sub>4</sub> ) <sub>2</sub> · A	444	yellow octahedral cryst.	Pt 43.96	44.10
5.	(aniline · H) <sub>2</sub> · A	596.2	dark yellow irreg. plates	Pt 32.74	32.99
6.	( <i>o</i> -toluidine · H) <sub>2</sub> · A · H <sub>2</sub> O	642.3	sparkling, yellow long needles	Pt 30.39	30.09
7.	( <i>m</i> -toluidine · H) <sub>2</sub> · A · H <sub>2</sub> O	642.3	sparkling yellow needles	Pt 30.39	30.52
8.	( <i>p</i> -toluidine · H) <sub>2</sub> · A	624.3	sparkling prisms	Pt 31.27	30.87
9.	( <i>m</i> -xylydine · H) <sub>2</sub> · A	652.3	yellow needles	N 4.49	4.80
10.	(pyridine · H) <sub>2</sub> · A	568.2	yellow irregular plates	Pt 29.92	29.60
11.	( <i>γ</i> -picoline · H) <sub>2</sub> · A	596.2	yellow hexagonal plates	N 4.29	4.36
12.	(3,4-lutidine · H) <sub>2</sub> · A	624.3	yellow rhomb. prisms	Pt 34.36	33.92
13.	(2,6-lutidine · H) <sub>2</sub> · A	624.3	yellow irregular prisms	Pt 32.74	32.50
14.	(3,5-dimethyl-2-ethyl-pyridine · H) <sub>2</sub> · A	680.2	yellow irregular cryst.	N 4.70	4.85
15.	(imidazole · H) <sub>2</sub> · A	546.1	yellow cryst. crops	Pt 31.27	31.33
16.	(benzimidazole · H) <sub>2</sub> · A · 2H <sub>2</sub> O	686.1	dark yellow prisms	N 4.49	4.12
17.	( <i>o</i> -oxy-chinoline · H) <sub>2</sub> · A · H <sub>2</sub> O	736.3	yellow irregular cryst.	N 4.49	4.70
18.	( <i>α, α'</i> -dipyridyl · H) · A	561.5	yellow irregular plates	Pt 28.70	28.43
19.	(diethylphenyl-phosphine · H) <sub>2</sub> · A	742.7	yellow dendrites	N 4.11	3.88
	A - [PtCl <sub>6</sub> ] <sup>2-</sup>			Pt 35.74	36.10
				Pt 28.45	28.30
				Pt 26.51	26.28
				N 3.80	4.15
				N 4.99	4.70
				Pt 26.30	26.45

and the second stage consists of the volatilization of KCl. In the first stage, up to 680°, the weight loss corresponds to exactly 2Cl<sub>2</sub>, and in the second stage, up to 860°, to 2 KCl.

The same two processes occur in the decompositions of the analogous Cs and Tl salts, but in these cases they do not appear separately in the TG curves; the redox reaction and the volatilization of CsCl or TlCl overlap each other.

This is quite easy to understand: the ionic radius increases in the sequence  $K^+ < Tl^+ < Cs^+$ , and the beginning of the thermal decomposition, i.e. of the above redox reaction, increases in the same sequence. According to the TG curves the decomposition of the K, Tl and Cs salts begins at about 450°, 540° and 600°C, respectively. On the other hand, the volatility of CsCl or of TlCl is much higher than that of KCl.

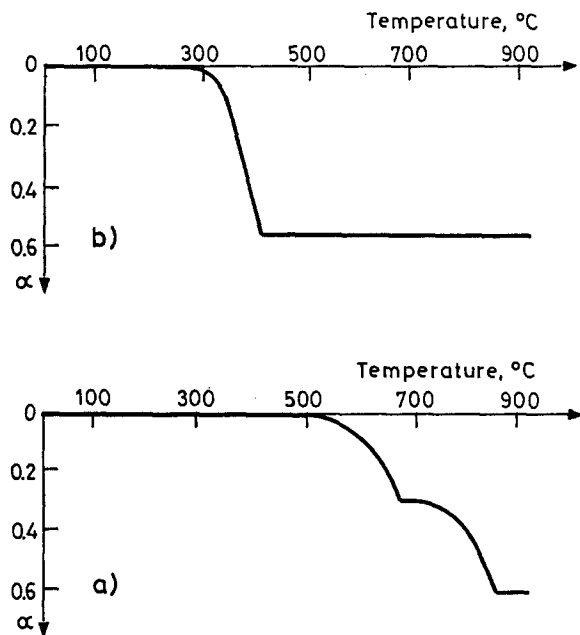
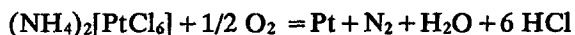


Fig. 1 TG curves of (a) K<sub>2</sub>[PtCl<sub>6</sub>]; (b) (NH<sub>4</sub>)<sub>2</sub>[PtCl<sub>6</sub>]

It is seen from Fig. 1b that the pyrolysis of the NH<sub>4</sub> salt occurs in a single stage and at lower temperature. This might be due to the reducing character of the outer sphere NH<sub>4</sub><sup>+</sup> ion, which diminishes the decomposition temperature. The products of the redox reaction are gaseous. Since the

reaction takes place in the presence of air, atmospheric oxygen may also participate in the reaction, which may be presumed to be as follows:



The pyrolyses of the other complexes are much more complicated and occur in 3, 4 or even 5 successive stages. Several examples are given in Figs 2–4.

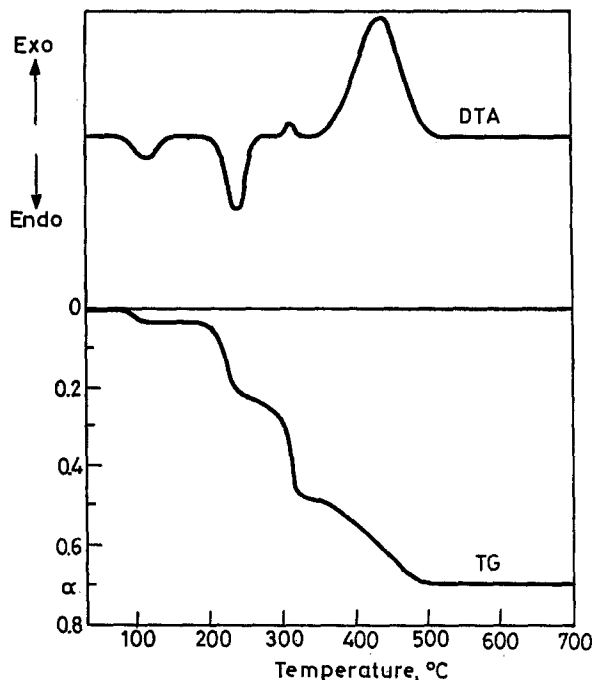


Fig. 2 TG and DTA curves of  $(m\text{-toluidine}\cdot\text{H})_2[\text{PtCl}_6]\cdot\text{H}_2\text{O}$

Figure 2 shows that in the first decomposition stage the *m*-toluidine derivative loses its crystallization water in an endothermic process. The second decomposition stage is also endothermic and the weight loss corresponds to one mole of *m*-toluidine hydrochloride. This is followed by two exothermic processes, without the formation of any well-defined stable intermediate. The process occurs with the participation of atmospheric oxygen and finally leads to metallic Pt as the only solid product.

The  $\gamma$ -picoline derivative contains no crystallization water; thus, its decomposition begins at higher temperature and occurs in 4 successive stages (Fig. 3). The first two stages are endothermic and the overall weight

loss slightly exceeds one mole of  $\gamma$ -picoline·HCl. The last two exothermic stages lead to the evolution of gaseous oxidation products and metallic Pt remains as solid residue.

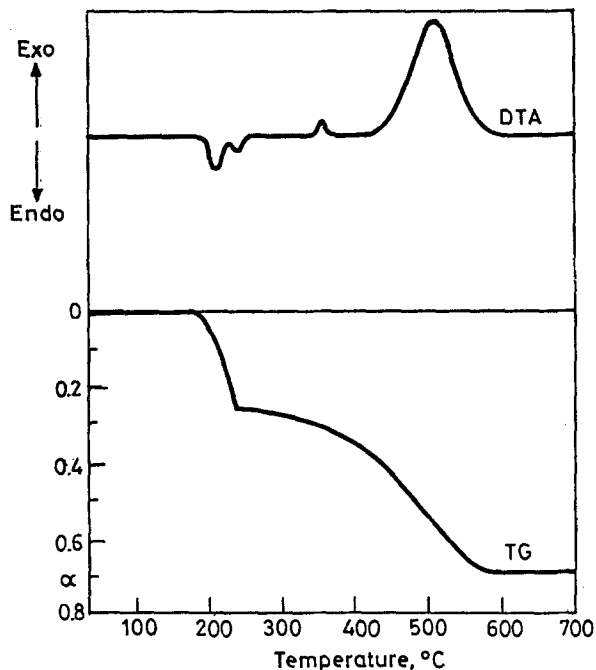


Fig. 3 TG and DTA curves of  $(\gamma\text{-picoline}\cdot\text{H})_2[\text{PtCl}_6]$

The phosphine derivative presented in Fig. 4, exhibits a lower thermal stability as compared to the amine derivatives. It decomposes in two endothermic stages, followed by a single exothermic one, without the formation of stable intermediates. The positions of the endothermic and exothermic peaks in the DTA curves of the amine and phosphine derivatives are given in Table 2.

Values given in parentheses are approximate ones. It is obvious that the deamination endothermic peak temperatures are generally situated between 200° and 250°C, although the second endothermic peak may sometimes appear at higher temperatures, up to 300°–350°C. The DTA curve of the phosphine derivative exhibits endothermic peaks at much lower temperatures. In most cases, the weight losses in the endothermic processes correspond to one mole of amine hydrochloride. This weight loss is sometimes higher and can reach even two moles of amine·HCl.

**Table 2** Endothermic and exothermic peak temperatures, °C

Complex salt No.	Endothermic		Exothermic
	Dehydration	Deamination	
5.	–	210, 258	383
6.	108	194, 230	448
7.	118	230	305, 418
8.	–	222	332
9.	–	290	496, 560
10.	–	210, 239	482
11.	–	208, 238	358, 510
12.	–	212, 242	383
13.	–	222	456
14.	–	215, 300	475
15.	–	220, 250	(450)
16.	65	228, 356	(450)
17.	95	178, 320	(400)
18.	–	218, 282, 315	(450)
19.	–	115, 160	332

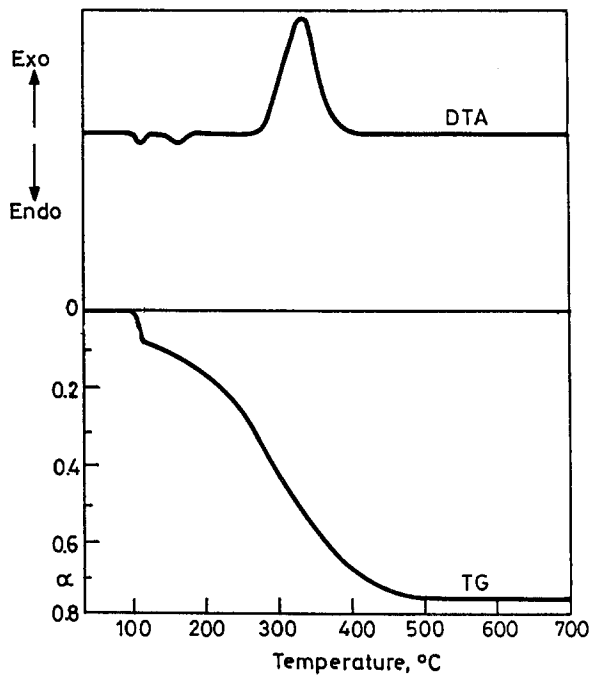
**Fig. 4** TG and DTA curves of (diethylphenylphosphine · H)<sub>2</sub>[PtCl<sub>6</sub>]

Table 3 Kinetic parameters derived from the TG curves

Complex No.	Stage*	<i>n</i>	<i>E</i> , kJ	lg <i>Z</i> **	$\tau_{0.1}$
1.	-2 Cl <sub>2</sub>	0.42	143.1	5.56	1.193
1.	-2 KCl	0.87	338.9	13.9	0.950
4.	overall	0.68	118.8	7.04	1.599
5.	end I	1.04	204.2	26.7	2.183
5.	end II	1.69	386.3	36.5	1.949
5.	ex	0.82	87.5	4.5	1.687
6.	end I	0.85	180.7	18.87	2.283
6.	end II	2.44	185.9	16.67	1.987
7.	end	0.43	183.0	16.03	2.045
7.	ex I	1.92	587.0	51.28	1.737
7.	ex II	1.31	103.3	5.26	1.536
8.	end	1.81	172.6	18.48	2.076
9.	end	0.54	126.3	9.62	1.949
9.	ex I	1.57	159.0	9.20	1.475
9.	ex II	2.67	805.7	50.40	1.245
10.	end II	1.94	770.1	77.30	1.978
10.	ex	2.50	324.4	20.70	1.383
11.	end I	1.66	378.8	40.0	2.124
11.	ex II	2.35	173.3	9.77	1.396
12.	end I	1.61	285.4	29.1	2.114
13.	end	1.53	636.2	65.6	2.067
14.	ex	1.52	211.3	13.2	1.469
16.	deh	1.01	139.0	18.3	3.001
16.	end I	1.61	545.8	53.3	1.984
16.	end II	0.34	183.9	12.9	1.654
17.	deh	1.31	234.4	31.8	2.790
17.	end I	1.68	278.2	30.6	2.280
18.	end I	-0.03	144.1	12.8	2.079
19.	end I	0.14	153.2	18.9	2.654
19.	end II	0.47	250.0	32.8	2.609

\* deh – endothermic dehydration; end – endothermic deamination; ex – exothermic; I, II – first or second value in Table 2

\*\* *Z* expressed in s<sup>-1</sup>

The exothermic processes occur above 300°C and are generally finished up to 450°–500°C when the weight of the sample equals the Pt content of the complex.



Some portions of the TG curves allow a kinetic analysis and the derivation of apparent kinetic parameters such as reaction order ( $n$ ), activation energy ( $E$ ) and pre-exponential factor ( $Z$ ). For this purpose, our 'nomogram method' [17–18] was used. The results obtained are presented in Table 3.

The same Table also gives the  $\tau_{0.1} = 10^3/T_{0.1}$  value where  $T_{0.1}$  is the absolute temperature at which the conversion attains  $\alpha = 0.1$ .

It can be seen, that the kinetic parameters vary in a large interval and their values cannot be correlated with the characteristics of the chemical process. Nevertheless, the  $\log Z$  values increase with increasing  $E$ , i.e. a kinetic compensation effect is observed. Through use of a linear regression, the parameters  $a$  and  $b$  of the linear compensation law

$$\log Z = a E + b$$

were derived. The above kinetic compensation is presumed to result from the Arrhenius equation for an isokinetic temperature [19, 20], with  $a = 1/2.3 R T_i$ , where  $T_i$  is the isokinetic temperature. If  $T_i$  is presumed to be practically equal to  $T_{0.1}$  [21], the compensation parameter  $a^* = \bar{\tau}_{0.1}/2.3 R$  can be calculated where  $\bar{\tau}_{0.1}$  is the mean value of  $\tau_{0.1}$ .

As one may expect, the larger the  $\tau_{0.1}$  range, the worse the  $\log Z$  vs.  $E$  linearization [21, 22].

Table 4 Kinetic compensation parameters

$T_{0.1}$ range, °C	$\rho$	$b$	$a$ , mole/kJ	$a^*$ , mole/kJ	$\Delta$ , %
60–566	0.9330	0.531	0.0886	0.1018	–12.96
60–111	0.9954	–1.824	0.1405	0.1444	– 2.70
105–208	0.9948	–2.549	0.1137	0.1138	– 0.09
208–240	0.9983	–2.134	0.1036	0.1047	– 1.06
302–353	0.9999	–4.060	0.0940	0.0872	+ 7.80
378–408	0.9996	–2.393	0.0735	0.0780	– 5.81
443–566	0.9978	–2.232	0.0657	0.0682	– 3.30

All the kinetic parameters presented in Table 3, except those relating to the volatilization of KCl, for which  $\tau_{0.1} = 769^\circ\text{C}$ , were processed via linear regression. Results are presented in Table 4, which contains not only the compensation parameters  $a$  and  $b$ , but also the correlation coefficient  $\rho$ , the 'theoretical' compensation parameter  $a^*$ , and the deviation  $\Delta$  of  $a$  from  $a^*$ . Obviously, the use of narrow  $T_{0.1}$  ranges entails the increase of  $\rho$ , indicating very good linearity and reduces the deviation  $\Delta$ . Therefore, the hypothesis

that the 'kinetic compensation effect' is merely a consequence of the use of the Arrhenius equation seems to be correct.

## Experimental

### *(amine·H)<sub>2</sub>[PtCl<sub>6</sub>]*

20 mmoles of the corresponding amine was treated with 10 ml 20% HCl and warmed for 10–15 minutes on a water bath. After cooling, the solution was treated with 2 mmoles of H<sub>2</sub>[PtCl<sub>6</sub>]·6 H<sub>2</sub>O in 10 ml aqueous solution. After standing for 15–30 minutes, the separated crystalline ammonium salts were filtered off, washed with ice-cooled water and dried in the air.

### *Analysis*

The platinum content was determined gravimetrically as metal after ignition at 800–900°C. The nitrogen content was determined by means of the micro-Dumas method.

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**Zusammenfassung** — Es wurden neunzehn Salze von Hexachlorplatinsäure mit monovalenten Metallen, aromatischen und heterocyclischen Aminen und Phosphinen hergestellt und mittels chemischer Analyse beschrieben. Mittels Derivatographie und DSC wurden die thermischen Eigenschaften dieser Komplexe untersucht. Es wird die Natur des Pyrolyseprozesses diskutiert. Anhand der TG-Kurven wurden kinetische Parameter für die einzelnen Schritte der thermischen Zersetzung ermittelt.