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Simultaneous thermal analysis/mass spectrometric investigations on the thermal behaviour of noble metal complexes

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Abstract

The results of investigations on the thermal behaviour of three selected noble metal complexes, performed by means of simultaneous thermal analysis/mass spectrometry are discussed The thermal analysis data, such as the initial temperatures for the beginning of the weight loss, the amounts of the weight loss, as well as the characteristic DTG and DTA temperatures, are tabulated and the simultaneously recorded electron impact mass spectra are interpreted. The temperature-dependent formation and cleavage of typical complex-structure-related substituents is described and established by the evaluation of the course of the corresponding ion-current intensities

INTRODUCTION

For many applications, the noble metal complexes of palladium, platinum and rhodium chloride are of great importance, especially with regard to catalytic reactions accompanied by a thermal treatment in the heterogeneous and homogenous catalysis of many chemical processes. In such processes, the thermal stability of the complex is of great interest.

EXPERIMENTAL

Noble metal complexes

The complexes investigated were diammonium chloropalladium, $[Pd(NH_3)_2Cl_2]$, ammonium hexachloroplatinate, $(NH_4)_2[PtCl_6]$, and ammonium hexachlororhodate, $(NH_4)_2[RhCl_6]$. The metal content of these complexes is 50.3% palladium, 43.9% platinum and 28.35% rhodium.

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Instrumental

The simultaneously thermal analysis/mass spectrometric instrument used consisted of a Netzsch STA 429 thermal analyser, a Balzers QMG 511 quadrupole mass spectrometer and a Digital Equipment PDP 11/23 + microcomputer.

The thermal analyser was equipped with a measuring device which registers the DTA and DTG curves. A linear temperature use of 5 K min^{-1} was applied in air atmosphere with samples weighing about 30 mg. Alumina oxide was used as a reference material.

Aluminium oxide tubes with holes in their bases were used as an interface for the pressure reduction between the thermal analyser and the mass spectrometer. The operating principle of the pressure reduction system (gas-inlet system) was described previously [1–7].

The mass spectra were recorded in temperature intervals of 10 K, the ionisation energy of the cross-beam ion source being 70 eV.

The software for the registration and evaluation of the mass spectrometric data is self-developed. The operating system of the microcomputer is RT 11 and the programming language is FORTRAN IV.

RESULTS AND DISCUSSION

Thermal analysis investigations

As we have reported earlier [8–13] the application of TA/MS to the investigation of the thermal behaviour and the determination of the thermal properties of metal complexes has proved to be very suitable.

A comparison of the initial temperatures for the beginning of the weight loss leads to the following thermal stability order for the complexes: Rh < Pd < Pt. The same result is obtained by comparing the values for the first maximum reaction rates and for the DTG peak temperatures.

For the palladium and platinum complexes, the thermal degradation in air occurs in one step. Considering the accuracy of the experimental technique, the sum of the weight loss and the metal residue is in the range of 100% (see Table 1). In contrast, the degradation of the rhodium complex is a multi-stage process under the same experimental and instrumental conditions. The sum of the weight loss and the metal residue amounts to only 92.4%. Further heating of the palladium complex results in an increase in weight of 8.3% due to the oxidation of the residual palladium. The thermal analysis data are listed in Table 1.

Mass spectrometric investigations

From the molecular structure of the compounds, it is clear that thermal treatment of the complexes results in successive cleavage, first of the

TABLE 1

Thermal analysis data of the noble metal complexes

	Pd complex	Pt complex	Rh complex
T_i (°C)	248	273	176
DTG_{p1}	331	400	241
DTG_{p2}	487		261
DTG_{p3}			357
DTG_{p4}			437
DTG_{p5}			665
DTA_{p1}	331, endo	312, endo	231, endo
DTA_{p2}		398, endo	261, endo
DTA_{p3}			357, endo
DTA_{p4}			423, endo
DTA_{p5}			448, exo
DTA_{p6}			673, exo
dm_1 (%)	49.2	56.2	3.2
dm_2 (%)	8.3 increase		3.5
dm_3 (%)			8.2
dm_4 (%)			29.3
dm_5 (%)			19.8
dm_{tot} (%)	40.9	56.2	64.0

ammonium and, second, of the chlorine ligands. To confirm this assumption which is based on the different types of chemical bonds present, the change in the corresponding ion-current intensities with temperature was investigated; that of the palladium compound is shown for example in Fig. 1.

From the course of the ion current intensity in the temperature region from ambient to 650 K (380 °C), it can be concluded that the ammonium

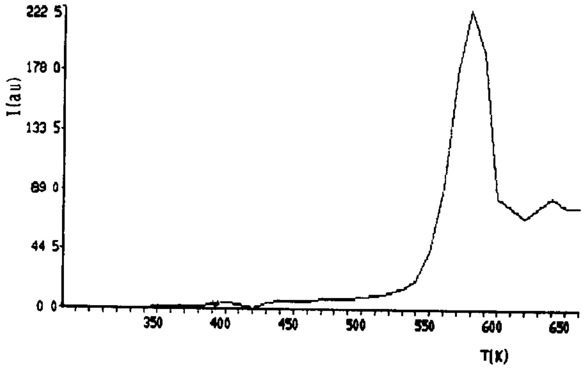

Fig 1. Cleavage of ammonium from the diammonium chloropalladium complex, depending on the temperature.

TABLE 2

Temperatures of the initial appearance and of the maximum intensities of chlorine cleavage

Complex	T_1 (K (°C))	T_{max1} (K (°C))	T_{max2} (K (°C))	T_{max3} (K (°C))
Palladium	550 (277)	600 (327)		
Platinum	570 (297)	670 (397)		
Rhodium	460 (187)	610 (337)sh	700 (427)	920 (647)

cations are released from the palladium complex at 350 K (77 °C). The maximum concentration in the gas phase was determined to occur at 580 K (303 °C). The initial temperatures for the platinum and rhodium catalysts are in the same range but their maximum intensities are shifted to higher temperatures: for the platinum complex, T_{max} is at 650 K (377 °C), and for ammonium hexachlororhodate, at 700 K (427 °C). It should be noted that all spectra are background-free because the application of a special software option permits the subtraction of all detected residual components from the mass spectrometer signal.

The same evaluation procedure was carried out for the determination of the chlorine loss from the metal complexes. The values of the initial detection temperatures and the maximum intensities of chlorine are summarised in Table 2.

For clarity and simplicity, the temperature dependent ion-current intensities of the chlorine and HCl cations corresponding with the natural abundance of the chlorine isotopes ^{35}Cl and ^{37}Cl in the ratio 3 : 1, were plotted. As an example, the curves for the rhodate compound are shown in Fig. 2.

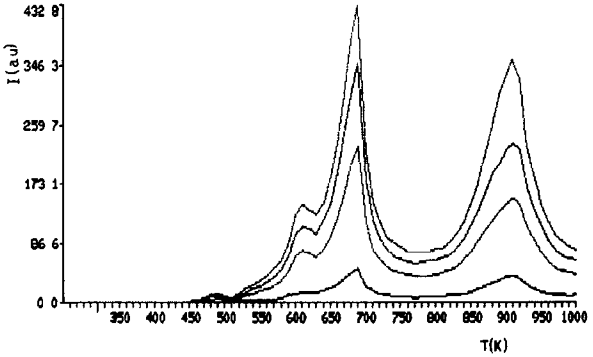

Fig. 2. Temperature-dependent course of the ion-current intensities of ^{35}Cl and ^{37}Cl, and of hydrogen chloride in the ratio of their natural abundance

On the basis of these results the fragmentation pathway for the palladium and platinum complexes can be interpreted as

$$[Pd(NH_3)_2Cl_2] \rightarrow PdCl_2 + 2NH_3$$

$$PdCl_2 \rightarrow Pd + Cl_2$$

$$Pd + 0.5O_2 \rightarrow PdO$$

$$(NH_4)_3[PtCl_6] \rightarrow PtCl_4 + 2NH_3 + 2HCl$$

$$PtCl_4 \rightarrow Pt + 2Cl_2$$

The thermal analysis results indicate that the degradation of the rhodium compound is more complex, with a multi-stage degradation pathway. However, the mass spectral data suggest that the subsequent weight losses from dm_1 to dm_4 can be regarded as a one-step reaction only. Thus, the degradation of the rhodium complex obtained is very similar to the above-mentioned pathways of the palladium and platinum complexes.

$$(NH_4)_3[RhCl_6] \rightarrow RhCl_3 + 3NH_3 + 3HCl$$

$$2RhCl_3 + 1.5O_2 \rightarrow Rh_2O_3 + 3Cl_2$$

A comparison between the theoretical weight loss data and the actual experimental values according to the degradation pathways for the three noble metal complexes is summarised in Table 3.

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TABLE 3

Comparison of the weight loss data of the palladium, platinum and rhodium complexes

		Weight loss (%)	
		Measured	Theoretical
Pd complex		−49.2	−49.7
		+8.3	+7.6
	total	−40.9	−42.1
Pt complex		−56.2	−56.1
Rh complex		−44.2	−43.4
		−19.8	−22.3
	total	−64.0	−65.7

REFERENCES

1 K.-H Ohrbach, W Klusmeier and A Kettrup, Thermochim. Acta, 72 (1984) 165.
2 A Kettrup, K -H. Ohrbach and G. Radhoff, in A. McGhie (Ed), Proc 13th North Am Therm. Anal. Soc. Conf., 1984, p. 449.
3 K -H Ohrbach, G. Radhoff and A. Kettrup, Thermochim. Acta, 85 (1985) 403.
4 K.-H Ohrbach and A. Kettrup, J. Polym. Degrad. Stab., 13 (1985) 99.
5 A. Kettrup, K.-H Ohrbach and G. Matuschek, Deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie, Forschungsbericht 356, Hamburg, 1985, 70 p.
6 K.-H Ohrbach, A. Kettrup and G. Matuschek, Proc. 4th Conf. on Indoor Air Quality and Climate, Oraniendruck, Vol. 3, Berlin, 1987, p 241.
7 A. Kettrup and K.-H. Ohrbach, in E Marti, H.R. Oswald and H.G. Wiedemann, (Eds), Angewandte Chemische Thermodynamik und Thermoanalytik, Birkhäuser Verlag, Basel, 1979, p. 103
8 K.-H Ohrbach, G. Radhoff and A. Kettrup, Fresenius' Z. Anal. Chem., 314 (1983) 398.
9 A Kettrup, K.-H. Ohrbach, G. Radhoff and W. Klusmeier, Thermochim. Acta, 74 (1984) 87
10 K.-H. Ohrbach, G. Radhoff and A. Kettrup, Int J. Mass Spectrom Ion Phys., 47 (1983) 189
11 K -H Ohrbach, G. Radhoff and A Kettrup, Thermochim. Acta, 67 (1983) 189.
12 K.-H. Ohrbach, G Radhoff and A Kettrup, Thermochim. Acta, 67 (1983) 197
13 K.-H. Ohrbach, G Radhoff and A Kettrup, J. Therm. Anal., 28 (1983) 155.