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THERMAL DECOMPOSITION OF TETRAAMINEPLATINUM(II) CHLORIDE BY SIMULTANEOUS TG/DTG/DTA/MS AND DIRECT INSERTION PROBE MASS SPECTROMETRY

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Simultaneous thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), and evolved gas analysis (EGA) by mass spectrometry (MS) have been used to determine the decomposition path for tetraamineplatinum(II) chloride and cis- and trans-diamineplatinum(II) chloride. Unequivocal identification of the evolved gases was done by direct insertion probe mass spectrometry.

The thermal decomposition of $(NH_3)_4PtCl_2$ occurred in two steps. The first was endothermic loss of two moles of ammonia producing a mixture of cis- and trans-diaamineplatinum(II) chloride. The second step was decomposition of the diamine complex to metallic Pt and N_2, HCl, and NH_4Cl. Reduction of Pt(II) to metallic Pt was coupled with oxidation of ammonia to molecular nitrogen and protons.

One method of preparing supported platinum catalysts is to load a predetermined amount of a suitable platinum complex onto the desired support and then to decompose the complex thermally to yield supported metallic platinum. We report the thermal decomposition reaction path for the pure complex.

Simultaneous thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), and evolved gas analysis (EGA) by mass spectrometry (MS) were performed. TG gives quantitative information on the change in sample mass as the sample is heated at a preset rate. DTA gives qualitative information on the endo- or exothermicity of transformations occurring during the thermal treatment. MS allows one to qualitatively analyze the vapor space above the sample during thermal treatment. In addition we also measured the derivative of the TG trace (DTG) during these experiments. This allows one to detect changes in the slope of the TG curve, occurring, for example when thermal events overlap, which might otherwise not be detected. Thus TG events are more clearly defined by using DTG.

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In addition, the complex was thermally decomposed in the solids insertion probe of a mass spectrometer to directly identify the gaseous species generated.

Experimental

General

Tetraamineplatinum(II) chloride, and cis- and trans-diamineplatinum(II) chloride were purchased from ALFA and used as received. House nitrogen, used in all thermal decomposition experiments, was further purified by passage through a molecular sieve (3A) dryer.

TG/DTG/DTA/MS

The equipment is comprised of three major components: quadrupole mass spectrometer (QMS), simultaneous thermal analyzer (STA), and gas sampling system. The STA and gas sampling system were purchased from Netzsch and consist of a Netzsch STA 429, Balzers vacuum flanges, and a dual fused alumina orifice sampling system. The mass spectrometer is a component system purchased from Extranuclear Laboratories. The major components are a cross beam ionizer, ionizer control, ELFS quadrupole mass filter, two high-Q heads for two mass ranges (1–100 and 1–500 amu), Channeltron 4700 multiplier, and Tektronix scope.

Our vapor sampling method is shown in Figure 1. It consists of two concentric fused alumina thimbles, each with a 50–100 micron orifice for continuous sampling of the vapor immediately above the sample. The pressure at the sample was approximately one atmosphere. When the sample chamber was at atmospheric pressure, the pressure between the two thimbles was maintained at 0.1–5 mbar using a mechanical pump; the pressure at the ion source was maintained at $5\text{–}50 \times 10^{-7}$ mbar with a diffusion pump and liquid nitrogen trap. The shutter (see Figure 1) was removed and replaced with an inlet system for MS calibration standards. The inlet system was supplied by Vacumetrics.

Thermal decompositions

Generally 75 to 200 mg of sample was weighed into a disposable fused alumina crucible. About 100 mg of α-Al_2O_3 was weighed into a similar reference crucible. For the pure compound decompositions, the furnace temperature was programmed to 350° at 10 deg/min then to 650° at 4.5 deg/min. Note that the temperatures for the thermal programs correspond to the furnace temperature and not to the sample temperature which lagged the furnace temperature 50–100°. However, the temperatures given in the results are the sample temperatures.

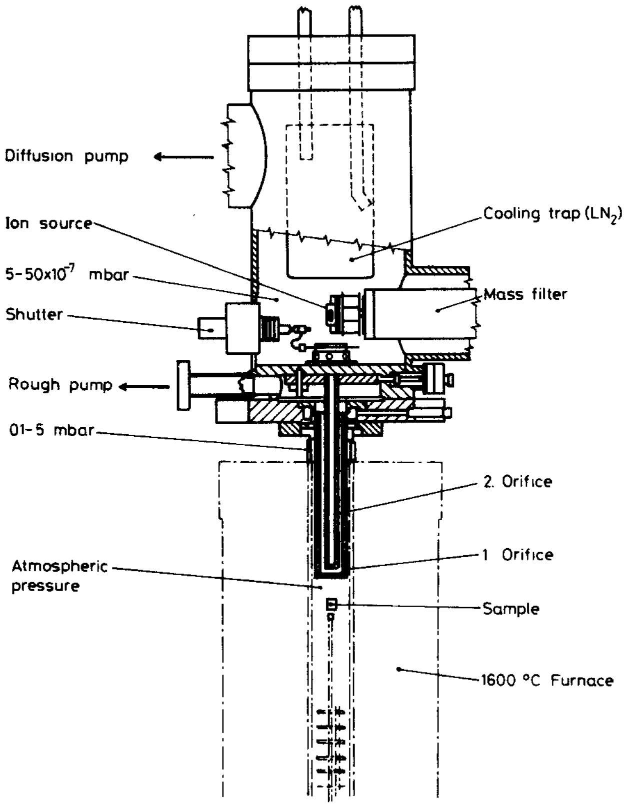

Fig. 1 Mass spectrometry gas sampling system

Direct insertion probe mass spectrometry

Approximately 1 mg of $(NH_3)_4PtCl_2$ was loaded in a glass capillary. The capillary was placed into the direct insertion probe tip of a Finnegan TSQ mass spectrometer operated in the single stage mode. The probe was heated at 40 deg/min to 350°. During the temperature program, mass spectra were recorded once each second from *m/e* 400 to *m/e* 10.

Results

$(NH_3)_4PtCl_2$

The TG/DTG/DTA/MS of tetraamineplatinum(II) chloride is shown in Figure 2. Two endothermic thermal events occurred. The first event occurred from 275° to

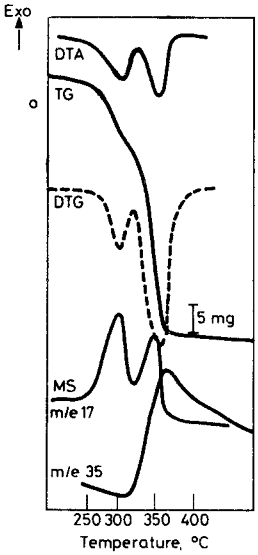

Fig. 2 TG/DTG/DTA/MS of $(NH_3)_4PtCl_2$

315° and resulted in a weight loss of 10.3%; the second occurred from 315° to 370° and resulted in a weight loss of 31.0%. The DTG trace indicates that the two events overlapped slightly. The MS traces show that only NH_3 was evolved during the first thermal event while NH_3 and Cl containing species were evolved simultaneously during the second thermal event. The "tail" associated with the *m/e* 35 response resulted from slow removal of chlorine containing species from the vacuum chamber as evidenced by a persistent, slowly decreasing *m/e* 35 background after removal of the sample.

Cis- and trans-$(NH_3)_2PtCl_2$

Only a single thermal event occurred during the decomposition of trans-$(NH_3)_2PtCl_2$, as shown in Figure 3. The mass change corresponded to a weight loss of 35.0% over the temperature range of 340° to 375°. The thermal decomposition of the cis isomer was similar to the trans isomer but was shifted to lower temperature by about 10–15°. The DTA traces for the cis- and trans-diamineplatinum(II) chloride and for the second thermal event in the decomposition of tetraamineplatinum(II) chloride are compared in Figure 4.

Direct insertion probe MS of $(NH_3)_4PtCl_2$

The relative ion intensities for *m/e* 17 (NH_3^+), *m/e* 28 (N_2^+) and *m/e* 36 (HCl^+) during temperature programming to 350° of $(NH_3)_4PtCl_2$ in the solids insertion

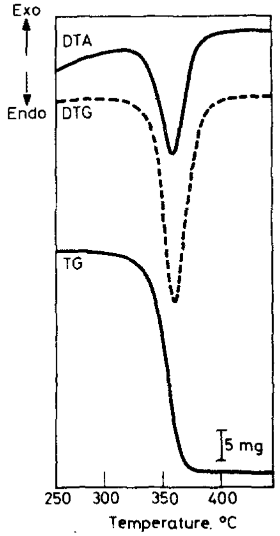

Fig. 3 TG/DTG/DTA of trans-$(NH_3)_2PtCl_2$

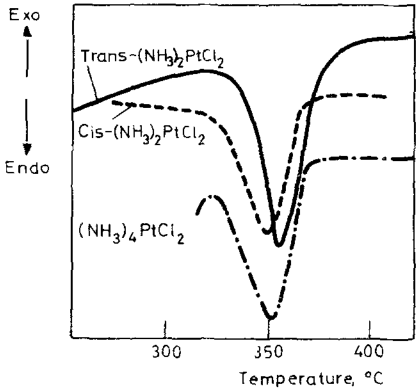

Fig. 4 DTA of cis- and trans-$(NH_3)_2PtCl_2$ and $(NH_3)_2PtCl_2$ from the decomposition of $(NH_3)_4PtCl_2$

probe of the mass spectrometer are shown in Figure 5. Ammonia was detectable from 250° to 350°, molecular nitrogen from 310° to 350°, and hydrogen chloride from 310° to 350°. The ion intensities of *m/e* 18 (H_2O^+) and *m/e* 32 (O_2^+) were also monitored to determine if water was interfering with the ammonia analysis and to estimate the contribution of air to the nitrogen response. In both cases the ratios of the *m/e* 18 to *m/e* 17 and *m/e* 32 to *m/e* 28 were less than 0.01 at the maxima. Thus, the contributions due to background air and water were negligible.

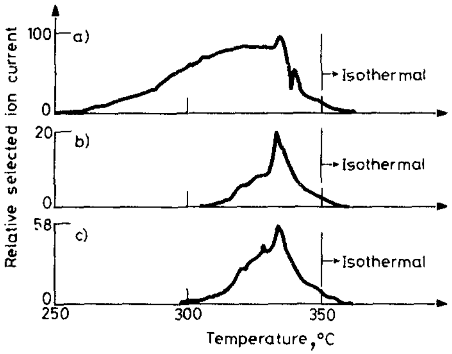

Fig. 5 Selected ion current versus temperature in the direct insertion probe of the mass spectrometer. Temperature was increased at 40 deg/min; ion currents were recorded once per second. A) *m/e* 17 (NH_3^+) B) *m/e* 28 (N_2^+) C) *m/e* 36 (HCl^+)

Discussion

Decomposition of amine platinum chloride complexes

$(NH_3)_4PtCl_2$: The thermal decomposition of $(NH_3)_4PtCl_2$ occurred in two steps. The first occurred from about 275° to 315° and involved the loss of two moles of ammonia, detected in the vapor phase by monitoring the *m/e* 17 (NH_3^+) intensity by mass spectrometry, per mole of the platinum complex. The resulting weight loss of 10.3% is in agreement with the theoretical weight loss of 10.2%. Thus, the first step of the thermal decomposition of the tetraamine complex is:

$$(NH_3)_4PtCl_2 \rightarrow (NH_3)_2PtCl_2 + 2NH_3 \qquad (1)$$

$(NH_3)_2PtCl_2$: The subsequent decomposition of $(NH_3)_2PtCl_2$ to metallic platinum occurred from 315° to about 370° and resulted in a weight loss of 31.0% based on the initial mass of the tetraamine complex. This is in agreement with the theoretical weight loss of 31.4%.

The DTG trace shown in Figure 2 did not return to baseline between the two thermal events indicating that the onset of the decomposition of the diamine complex overlapped slightly with the decomposition of the tetraamine complex. Thus the assignment of 315° for the onset of the decomposition of the diamine complex is somewhat lower than the 340° onset observed for the pure diamine (Figure 3).

The analysis of the evolved gases by mass spectrometry showed that ammonia (*m/e* 17) is evolved during both steps in the decomposition. Ammonia and a chlorine containing specie(s) were evolved simultaneously during the second step (decomposition of the diamine complex) and the onset of evolution of both ammonia (NH_3^+) and chlorine (Cl^+) occurred at the same temperature. Thus the decomposition of diamineplatinum(II) chloride does not lead to the formation of a stable $PtCl_2$ intermediate.

Since chlorine was observed by monitoring the *m/e* 35 response (Cl^+), the actual chlorine containing specie or species may have been Cl_2, HCl, and/or NH_4Cl. In fact, we cannot rule out the possibility that the ammonia response (*m/e* 17) was derived from NH_4Cl during the decomposition of the diamine complex especially since the vapor pressure of NH_4Cl approaches one atmosphere at approximately 340°. (We gratefully acknowledge the reviewer for this information.)

Since the complex ultimately decomposes to metallic platinum, the reduction of Pt(II) to Pt(0) must be accompanied by either the oxidation of chloride to molecular chlorine or the oxidation of ammonia to molecular nitrogen and protons. The former mechanism would yield molecular chlorine while the latter would yield hydrogen chloride in addition to N_2. Paulik et al. [1], have proposed that the decomposition of the diamine complex yields molecular nitrogen and HCl according to:

$$3(NH_3)_2PtCl_2 \rightarrow 3Pt + N_2 + 4NH_3 + 6HCl \tag{2}$$

with the reduction of platinum being coupled to ammonia oxidation:

$$3Pt^{2+} + 6e^- \rightarrow 3Pt \tag{3}$$

$$2NH_3 \rightarrow N_2 + 6e^- + 6H^+ \tag{4}$$

HCl is then formed by the reaction of protons and chloride.

The alternative is:

$$(NH_3)_2PtCl_2 \rightarrow Pt + 2NH_3 + Cl_2 \tag{5}$$

with the reduction of platinum being coupled to chloride oxidation:

$$Pt^{2+} + 2e^- \rightarrow Pt \tag{6}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{7}$$

While it is true that oxidation of ammonia is thermodynamically favored over oxidation of chloride ion, we could not be certain that the decomposition path was not kinetically controlled. The mechanistic conclusions of Paulik et al., hinge on the observation that no iodine was released from an aqueous solution of KI and H_2SO_4 upon passing the evolved gases from the thermal decomposition of $(NH_3)_4PtCl_2$ through the solution. Any molecular chlorine would have been reduced to chloride and the iodide oxidized to molecular iodine. Thus, they concluded that molecular nitrogen must have been produced by ammonia oxidation. However, no direct observation of molecular nitrogen was possible in their experiments since N_2 was used in the purge gas. We became concerned that the gases evolved during TG experiments could further react at catalytically active metallic platinum sites; especially since poor mass transport conditions usually exist within TG sample holders. Two potentially interfering reactions are possible which could complicate interpretation of the origin of evolved gases. The first is the well known [2–7] Pt catalyzed decomposition of ammonia to molecular nitrogen and molecular hydrogen. The second is the combustion of molecular hydrogen and molecular chlorine to produce HCl. This reaction could have been initiated at metallic platinum sites within the decomposing sample. It is possible that Paulik et al., did not observe molecular chlorine because of its conversion to HCl.

A direct observation of the evolved gases under conditions minimizing the possibility of secondary reactions was necessary to unequivocally identify the evolved gases. Direct insertion probe mass spectrometry is ideally suited for this since a very small sample is placed in the vacuum chamber within a centimeter of the ionizing section of the mass spectrometer. By heating the sample at a controlled rate we were able to identify the evolved gases instantaneously.

Ammonia (*m/e* 17) was detected at a probe temperature of 250°. As the temperature increased the rate of ammonia production increased. No other evolved gases were detected from 250° to 300° which confirms that the first step in the decomposition is loss of two moles of ammonia per mole of tetraamine complex. At about 310° HCl and N_2 were detected directly, confirming the mechanism proposed by Paulik et al.; reduction of Pt(II) is coupled to oxidation of ammonia to molecular nitrogen and protons which combine with chloride to give HCl.

Cis- and trans-$(NH_3)_2PtCl_2$: The thermal decompositions of the cis and trans isomers were measured to determine the relative stability of the isomers and to determine if there was a preferred isomeric product in the first step of the decomposition of the tetraamine complex.

The thermal decomposition of trans-diamineplatinum(II) chloride (Figure 3) occurred in a single step from about 340° to 375°.

The observed weight loss of 35.0% is in agreement with the theoretical value of 35.0% calculated for decomposition to platinum metal. The onset of decomposition of the cis isomer occurred at a temperature 10–15° lower than the trans isomer, which shows that the trans isomer is slightly more stable. Note that these results were measured with samples of nearly identical physical properties, i.e., sample size, particle size, etc., thus, the difference in decomposition temperature was indicative of a real difference in stability.

Comparison of the DTA traces of cis- and trans-$(NH_3)_2PtCl_2$ with the DTA trace of the second step in the decomposition of the tetraamine complex (Figure 4) reveals that the maximum in the DTA trace of the tetraamine complex falls between the maxima for the two isomeric diamine complexes. Thus, the tetraamine decomposed to a mixture of the cis and trans isomers.

Summary

The thermal decomposition of tetraamineplatinum(II) dichloride occurs in two endothermic steps:

STEP 1: $(NH_3)_4PtCl_2 \rightarrow (NH_3)_2PtCl_2 + 2NH_3$

STEP 2: $(NH_3)_2PtCl_2 \rightarrow Pt + N_2 + 4NH_3 + 6HCl$

The first step occurs from 275° to 315°; the second from 315° to 370°. The diamine produced in the first step is a mixture of the cis and trans isomers. Analysis of the evolved gases by direct insertion probe mass spectrometry unequivocally established the gaseous products for Steps 1 and 2.

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References

1 J. Paulik and F. Paulik, "Thermal Analysis: Part A. Simultaneous Thermoanalytical Examinations by Means of the Derivatograph" in Wilson & Wilson's Comprehensive Analytical Chemistry, V. 12, G. Svehla, Ed., Elsevier, New York, 1981, pp. 45–47.
2 S. R. Logan and C. Kemball, Trans. Faraday Soc., 56 (1960) 144.
3 L. O. Apelbaum and M. I. Temkin, Zhur. Fiz. Khim., 33 (1959) 2697.
4 A. J. B. Robertson and E. M. A. Willhoft, Trans. Farad. Soc., 63 (1967).
5 C. E. Melton and P. H. Emmett, J. Phys. Chem., 68 (1964) 3318.
6 J. K. Dixon, J. Am. Chem. Soc., 53 (1931) 2071.
7 C. N. Hinshelwood and R. E. Burk, J. Chem. Soc., 127 (1925) 1105.

Zusammenfassung — Simultane Thermogravimetrie (TG), derivative Thermogravimetrie (DTG), Differentialthermoanalyse (DTA) und Analyse der entwickelten Gase (EGA) durch Massenspektrometrie (MS) wurden zur Bestimmung des Reaktionsverlaufs bei Zersetzung von Tetraminplatin(II)-chlorid sowie cis- und trans-Diaminplatin(II)-chlorid herangezogen. Die eindeutige Identifizierung der entwickelten Gase erfolgte durch Massenspektrometrie mit direkter Probeneinführung. Die thermische Zersetzung von $(NH_3)_4PtCl_2$ erfolgt in zwei Schritten. Der erste ist die endotherme Abspaltung von zwei Mol Ammoniak unter Bildung eines Gemisches von cis- und trans-Diamin-platin(II)-chlorid. Der zweite Schritt ist die Zersetzung des Diaminkomplexes zu metallischem Pt, H_2, HCl und NH_4Cl. Die Reduktion von Pt(II) zu metallischem Pt ist mit der Oxydation von Ammoniak zu molekularem Stickstoff und Protonen gekoppelt.

Резюме — Совмещенные методы ТГ-, ДТГ-, ДТА-, АВГ- и масс-спектрометрии были использованы для определения путей разложения тетрааминоплатина(II)хлорида и цис- и транс-диаминоплатина(II)хлорида. Однозначная идентификация выделяющихся газов была проведена прямым введением пробы в масс-спектрометр. Термическое разложение $(NH_3)_4PtCl_2$ протекает в две стадии. Первой стадией разложения является эндотермическая потеря двух молей аммиака с образованием смеси цис- и транс-$(NH_3)_2PtCl_2$. Второй стадией является разложение диаминового комплекса до металлической платины, азота, хлористого водорода и хлористого аммония. Восстановление двухвалентной платины до металлической сопровождается окислением аммиака до молекулярного азота и протонов.