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THE THERMAL DECOMPOSITION OF METAL COMPLEXES—XIII

SOME TETRAMMINEPALLADIUM(II) COMPLEXES

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Abstract—The thermal dissociation of the palladium(II) tetrammine-complexes, $[Pd(NH_3)_4]X$ (where X is 2Cl, 2Br, 2I, 2NO₃, and SO₄), was studied by thermogravimetry, DTA, GE, and by analysis of the pyrolysis products. The complexes, except for the nitrate and sulphate, dissociated to give the *trans*-diammine-complexes, $[Pd(NH_3)_2X]$. The diammine-iodide and bromide complexes dissociated to give the corresponding anhydrous metal halides, PdX₂. The stoicheiometry for the thermal dissociation of the $[Pd(NH_3)_2X_2]$ complexes, where X was Cl, Br, and I, was determined.

ALTHOUGH a number of investigations have been concerned with the thermal dissociation of various platinum(II) and (IV) ammine complexes, the analogous palladium complexes have been little studied. NIKOLAEV and RUBINSHTEIN⁽¹⁾ studied the thermal dissociation and thermal isomerization of $[Pd(NH_3)_4][PdCl_4]$, $[Pd(NH_3)_4][PtCl_4]$, and $[Pd(NH_3)_2Cl_2]$ (in mixtures with other complexes), by DTA (thermography). MURAVEISKAYA and CHERNYAEV⁽²⁾ studied the thermal decomposition of *trans* $[Pd(NH_3)_2NO_2Cl]$. It was found that this complex decomposed violently between $212-224^{\circ}C.$, accompanied by a vigorous evolution of gases.

To study the similarities between the thermal decomposition of the tetramminepalladium(II) and platinum(II) complexes,^(3,4) the tetramminepalladium(II) complexes were prepared and their thermal properties studied by thermogravimetry, differential thermal analysis, and gas evolution analysis. To determine the stoicheiometry of the pyrolysis reactions, an analysis of the decomposition products was also attempted.

EXPERIMENTAL

Thermobalance. The automatic recording thermobalance has previously been described.⁽⁵⁾ The sample sizes ranged in weight from 20 to 65 mg and were pyrolysed in a static air atmosphere at a heating rate of about 7°C per min. The sample was contained in an uncovered No. 00000 Coors porcelain crucible during the pyrolysis reaction.

DTA and GE Apparatus. This apparatus has previously been described.⁽⁶⁾ Sample sizes ranged in weight from 20 to 60 mg and were pyrolysed in a dynamic helium atmosphere at a furnace heating rate of about 10°C per min. The sample was contained in a small uncovered Inconel cup during the pyrolysis reaction.

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Stoichiometry of pyrolysis reaction. The pyrolysis apparatus has previously been described.⁽⁷⁾ From 100 to 225 mg of sample was pyrolysed in a dynamic helium atmosphere (\sim 15 ml per min. flow rate) at a heating rate of 5°C per min. The evolved pyrolysis gases were collected in a bubbler tube containing standard 0.05 N hydrochloric acid, which was then back titrated with standard 0.05 N sodium hydroxide solution. Further analysis for ammonia (as NH₄⁺ salts) from the above solution was made by use of the Kjeldahl method. The ammonium salts which were retained as solids in the furnace were removed by dissolution in water or dilute hydrochloric acid and analyzed for ammonium content by the Kjeldahl method. The amount of residue remaining in the sample container was determined by weighing.

Nitrogen and hydrogen were detected in the pyrolysis products in a qualitative manner by use of a Consolidated Engineering Corp. Model 21-620 mass spectrometer. The heated sample chamber has previously been described.⁽⁸⁾

Preparation of complexes. The *trans*-diammine-complexes, $[Pd(NH_3)_2X_2]$ (where X = Cl, Br and I) were prepared from the corresponding PdX₂ salts as previously described.⁽⁹⁻¹¹⁾ The *trans* $[Pd(NH_3)_2(NO_3)_2]$ was prepared by treating $[Pd(NH_3)_4](NO_3)_2$ repeatedly with nitric acid and evaporating to dryness. The $[Pd(NH_3)_2SO_4]$ was prepared from $[Pd(NH_3)_2Cl_2]$ by treatment with Ag₂SO₄ in aqueous solution.

The tetrammine-complexes, $[Pd(NH_3)_4]X_2$ (X = Cl, Br, and I) were prepared by passing gaseous ammonia through aqueous solutions of the diammine-complexes at room temperature. The nitrate complex, $[Pd(NH_3)_4](NO_3)_2$, was prepared by treatment of $[Pd(NH_3)_4]Cl_2$ with AgNO₃. The complex, $[Pd(NH_3)_4]SO_4 H_2O$, was prepared in a similar manner by treatment of $[Pd(NH_3)_4]Cl_2$ with Ag₂SO₄.

All of the complexes were analysed for palladium content by ignition of the compounds to palladium metal at 800°C. for two hr and for ammonia content by the Kjeldahl method. The results of the analyses are given in Table 1.

| Compound | Pd (%) | | NH ₃ (%) | |
|---|--------|-------|---------------------|-------|
| | Calc. | Found | Calc. | Found |
| $[Pd(NH_3)_4]Cl_2$ | 43-41 | 42.9 | 27.80 | 27.4 |
| [Pd(NH ₃) ₄]Br ₂ | 31.82 | 32.8 | 20.37 | 20.0 |
| $[Pd(NH_3)_4]I_2$ | 24.84 | 24.8 | 15.90 | 15.5 |
| $[Pd(NH_3)_4](NO_3)_2$ | | _ | 22.82 | 22.5 |
| [Pd(NH ₃) ₄]SO ₄ | 39.32 | 39.1 | 25.18 | 25.6 |
| [Pd(NH ₃)₄]SO₄·H ₂ O | 36.86 | 37.3 | 23.60 | 23.6 |

TABLE 1.—COMPOSITION DATA FOR PALLADIUM COMPOUNDS

RESULTS AND DISCUSSION

Weight-loss studies. The weight-loss curves of the tetrammine-complexes, $[Pd(NH_3)_4]X$ (where X = 2Cl, 2Br, 2I, 2NO₃, and SO₄), are given in Fig. 1.

Except for the nitrate and sulphate complexes, all of the tetrammine-complexes evolved two moles of ammonia per mole of complex to give the *trans*-diammine-complexes, $[Pd(NH_3)_2X_2]$. This first step in the thermal decomposition sequence can be represented by:

$$[Pd(NH_3)_4]X_2(s) \rightarrow t-[Pd(NH_3)_2X_2](s) + 2NH_3(g)$$

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The minimum temperatures at which the diammine-weight-levels were attained, were: chloride, 185° C.; bromide, 180° C.; and iodide, 115° C. This thermal behaviour is similar to that found for the tetrammineplatinum(II) chloride complex.^(3,4) The temperature at which the latter diammine-complex is formed was 260° C;⁽⁴⁾ somewhat higher than that found here for the palladium(II) complexes.



FIG. 1.—Weight-loss curves of [Pd(NH₃)₄]X₂ complexes.

- A. [Pd(NH₃)₄]Cl₂ (46.0 mg)
- B. $[Pd(NH_3)_4]Br_2 (50.4 \text{ mg})$
- C. $[Pd(NH_3)_4]I_2$ (36.8 mg)
- D. $[Pd(NH_3)_4](NO_3)_2 (30.2 \text{ mg})$
- E. $[Pd(NH_3)_4]SO_4 H_2O (33.1 mg)$

The tetrammine-iodine and bromide complexes showed evidence for the formation of the anhydrous palladium(II) halides, as well, by the loss of two additional moles of ammonia from the diammine-complexes. The temperatures at which the palladium(II) halide weight-levels began were: PdI_2 , $210^{\circ}C$.; and $PdBr_2$, $360^{\circ}C$.

The tetrammine- nitrate and sulphate complexes did not form diammine-intermediates but instead, decomposed directly to palladium metal residues. In the case of $[Pd(NH_3)_4]SO_4 \cdot H_2O$, the water was evolved first, the process being completed at about $180^{\circ}C$.

Perhaps the most interesting region in the weight-loss curves, chemically speaking, was that due to the dissociation of the diammine-complexes to give a residue of palladium and other pyrolysis products. The stoicheiometry of this reaction was determined for $[Pd(NH_3)_2Cl_2]$, $[Pd(NH_3)_2Br_2]$ and $[Pd(NH_3)_2I_2]$, and will be discussed later in this paper.

DTA and GE studies. The DTA curves of the tetrammine-complexes are given in Fig. 2.

The DTA curves for the $[Pd(NH_3)_4]X_2$ (X = Cl, Br and I) complexes, under s helium, showed the same reactions, in general, as were found in the air atmosphere weight-loss studies. The curves were characterized by two endothermic peaks; one peak was due to the deamination reaction (loss of 2 moles of ammonia), while the other was due to either the total disruption of the diammine-complex ($[Pd(NH_3)_2Cl_2]$), or to the loss of two additional moles of ammonia to form the anhydrous palladium(II) halides ($[Pd(NH_3)_2Br_2]$ and $[Pd(NH_3)_2I_2]$). The peak maxima temperatures for the first deamination reaction increased in the order: iodine, $110^{\circ}C <$ bromide, $150^{\circ}C <$ chloride, $180^{\circ}C$.



E. $[Pd(NH_3)_4](NO_3)_2$

The nitrate complex, $[Pd(NH_3)_4](NO_3)_2$, decomposed in a very violent manner and gave only a single exothermic peak, with a peak maximum temperature of 245°C. This behavior was similar to that of other cobalt(II) and (III),^(7,12) chromium (III),⁽¹³⁾ and platinum(II) and (IV)⁴ complexes containing ammonia in the coordination sphere and nitrate ions in the ionization sphere.

The DTA curve of $[Pd(NH_3)_4]SO_4 H_2O$ showed the expected endothermic peak for the deaquation reaction (at 175°C), followed by the decomposition of the anhydrous $[Pd(NH_3)_4]SO_4$ complex in the 250–350°C region. The dissociation of the anhydrous complex appeared to consist of a number of consecutive reactions, judging from the shoulder peaks observed. The nature of these reactions is not known.

The gas evolution (GE) curves of the complexes are not reproduced here. Each DTA curve peak also gave a corresponding GE peak, indicating that a gaseous product was evolved in the reaction.

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Stoicheiometry of reaction. Since the tetrammine-complexes dissociated to form the diammine-complexes, $[Pd(NH_3)_2X_2]$, the stoicheiometry of the dissociation of these latter complexes was determined. Taking X to be chloride, bromide, and iodide, it was found that each dissociated in a different manner. The simplest decomposition reaction was that found for the iodide complex, $[Pd(NH_3)_2I_2]$, or:

$$t$$
-[Pd(NH₃)₂I₂](s) $\xrightarrow{250^{\circ}C}$ PdI₂(s) + 2NH₃(g)

The PdI_2 , on heating to higher temperatures, gave a residue of palladium, with the evolution of iodine.

By proper choice of pyrolysis temperature, the thermal decomposition stoicheiometry for $[Pd(NH_3)_2Br_2]$ should be similar to that found for $[Pd(NH_3)_2I_2]$. However, this was not found to be the case, probably because of the partial reaction of ammonia with the PdBr₂. The reaction stoicheiometry found corresponded to the equation:

$$5t-[Pd(NH_3)_2Br_2](s) \xrightarrow{430^\circ C} 4PdBr_2(s) - Pd(s) + 2NH_4Br(s) + 7NH_3(g) + \frac{1}{2}N_2(g) + \frac{1}{2}H_2(g)$$

The nitrogen and hydrogen in the pyrolysis products were only detected in a qualitative manner. The palladium metal in the residue must be formed as a result of the reaction of ammonia with $PdBr_2$.

The chloride complex, $[Pd(NH_3)_2Cl_2]$, decomposed in a somewhat different manner. From the weight-loss curve it is seen that anhydrous $PdCl_2$ is not formed; instead, the diammine-complex dissociated directly to palladium metal. The reaction stoicheiometry corresponded closely to the equation:

$$5t-[Pd(NH_3)_2Cl_2](s) \xrightarrow{430^{\circ}C} 5Pd(s) + 6NH_4Cl(s) + 4HCl(g) + 2N_2(g) + H_2(g)$$

Again, nitrogen and hydrogen were only detected qualitatively.

The data for the reaction stoicheiometry studies are given in Table 2. It should

| Sample (mM) | NH ₃ (mM) | NH ₃ /complex ratio | NH₄Br (mM) | NH₄Br/complex ratio | Residue (%) |
|--------------------|-------------------------|-----------------------------------|--------------------|----------------------------|--|
| $[Pd(NH_3)_2Br_2]$ | | | | | |
| 0.438 | 0.608 | 1.39 | 0.182 | 0.416 | 80.1 |
| 0.526 | 0.726 | 1.38 | 0.227 | 0.431 | 80.0 |
| Calculated: | | 1.40 | | 0.40 | 78·0 |
| $[Pd(NH_3)_2I_2]$ | | | | | |
| 0.243 | 0.475 | 1.95 | | | 90.7 |
| 0.541 | 1.040 | 1.92 | | | 90.9 |
| Calculated : | | 2.0 | | | 91.4 |
| Sample | HCI | HCl/complex | NH ₄ Cl | NH ₄ Cl/complex | Residue |
| (mM) | (mM) | ratio | (m M) | ratio | $\left(\begin{array}{c} 0 & 0 \\ 0 & 0 \end{array} \right)$ |
| $[Pd(NH_3)_2Cl_2]$ | | | | | |
| 0.648 | 0.517 | 0.798 | 0.763 | 1.18 | 50.3 |
| 0.557 | 0.438 | 0.786 | 0.688 | 1.24 | 51-1 |
| Calculated: | | 0.80 | | 1.20 | 50-3 |

TABLE 2.—REACTION STOICHEIOMETRY DATA

be emphasized that the reaction stoicheiometries determined here may only apply to this set of experimental conditions such maximum temperature, heating rate, helium flow-rate, and so on. Changing these conditions may well change the decomposition stoicheiometry.

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