CONTRIBUTION FROM UNION CARBIDE RESEARCH INSTITUTE,
TARRYTOWN, NEW YORK

The Chemistry of Platinum Hexafluoride. II. Reactions with Chlorine Trifluoride, Bromine Pentafluoride, and Tetrafluorohydrazine

BY F. P. GORTSEMA AND R. H. TOENISKOETTER

Received June 3, 1966

Platinum hexafluoride reacts with chlorine trifluoride to give chlorine pentafluoride and the solid ClF_3PtF_5. The infrared spectrum indicates that ClF_3PtF_5 exists in the ionic form $ClF_2{}^+PtF_6{}^-$. Platinum hexafluoride reacts with bromine pentafluoride to give fluorine and a black viscous liquid, but no higher bromine fluorides are formed. Tetrafluorohydrazine and platinum hexafluoride react to give nitrogen trifluoride and PtF_{4-5}.

Introduction

Several adducts of halogen fluorides with the higher platinum fluorides have been reported. Among these is the solid complex $(BrF_3)_2PtF_4$, which was prepared by the reaction of bromine trifluoride with platinum tetrafluoride or platinum pentafluoride.[1] Bartlett and Lohmann obtained the adduct ClF_3PtF_5 by the reaction of chlorine trifluoride with platinum pentafluoride[1] or dioxygenyl hexafluoroplatinate,[2] and they found also that platinum pentafluoride, but not platinum tetrafluoride, formed with iodine pentafluoride the solid IF_5PtF_5. Platinum tetrafluoride, however, did add selenium tetrafluoride to form the compound $(SeF_4)_2PtF_4$.[1]

Weinstock, *et al.*,[3] observed that platinum hexafluoride readily fluorinated bromine trifluoride to give bromine pentafluoride. This reaction also produced a black, viscous liquid which was not identified.

In part I of this work[4] we described the reactions of platinum hexafluoride with various nitrogen oxides and oxyfluorides. Although platinum was reduced in those reactions, no perfluorinated products other than elemental fluorine were produced. In the present paper, we report the results of a study of the reactions of platinum hexafluoride with chlorine trifluoride, tetrafluorohydrazine, and bromine pentafluoride.

Experimental Section

The metal vacuum system and the procedure for the preparation and handling of platinum hexafluoride, as well as the details of the techniques used for the X-ray diffraction, infrared, and density measurements, are described in part I.[4] For reactions involving tetrafluorohydrazine and platinum hexafluoride, the Teflon valve seat of the reactor was replaced with one of copper to avoid the formation of carbon tetrafluoride.

Chemicals.—Chlorine trifluoride and bromine pentafluoride were obtained from the Matheson Company and were purified by trap to trap distillation. The chlorine trifluoride in addition was passed through an activated sodium fluoride pellet column to absorb hydrogen fluoride.[5] Data on the purified gases agreed well with published values for vapor pressure[6-8] and infrared spectra.[9,10] Research grade tetrafluorohydrazine was obtained from Air Products and Chemicals Co., Inc., and was used without further purification. The supplier's analysis indicated the following composition in weight per cent: N_2F_4, 99.95; N_2, 0.04; H_2O, 0.01; NO, nil. The infrared spectrum of this compound was in excellent agreement with the reported spectrum.[11]

Reactions of Platinum Hexafluoride and Chloride Trifluoride.—Platinum hexafluoride (3.11 mmoles, 1.048 g) and chlorine trifluoride (4.66 mmoles) were condensed at −196° into an evacuated nickel reactor. The mixture was warmed slowly from −196 to 25° over a period of 12 hr. The gaseous product was chlorine pentafluoride (1.51 mmoles), which was identified by its infrared spectrum.[12] No unchanged chlorine trifluoride was found. The bright yellow solid product weighed 1.190 g, corresponding to 3.11 mmoles of ClF_3PtF_5.

Anal. Calcd for ClF_3PtF_5: Pt, 51.0; F, 39.7; Cl, 9.27. Found: Pt, 50.4; F, 37.8; Cl, 9.30.

The adduct ClF_3PtF_5 is very hygroscopic and must be handled under strictly anhydrous conditions. It reacts violently with water to give a yellow solution which evolves vile-smelling gases.

The X-ray diffraction pattern of ClF_3PtF_5 consisted of many sharp lines, but it could not be indexed on the basis of any simple cell. Epr measurements showed the material to be paramagnetic.

Infrared spectra were measured on thin films formed by carrying out the reaction in a nickel infrared cell with silver chloride windows. A strong absorption band at 561 cm^{-1} with two shoulders at 529 and 505 cm^{-1} constituted the entire spectrum between 5000 and 350 cm^{-1}. Spectra were not obtained from mulls because the compound reacts explosively with Nujol.

Addition of fluorine to the reaction system at 25° had no effect on the course of the reaction, the products being only chlorine pentafluoride and ClF_3PtF_5. Lower temperatures, or an excess of chlorine trifluoride, also had no effect. For example, when a mixture of 2.30 mmoles of platinum hexafluoride and 8.90 mmoles of chlorine trifluoride was held at −78° for 18 hr, the gaseous reaction mixture consisted of 1.05 mmoles (91% yield) of chlorine pentafluoride and 5.34 mmoles of unchanged chlorine trifluoride. Recovery of the excess chlorine trifluoride from the reactor at −78° required continuous pumping for 6.5 hr. The slowness of this recovery may indicate a weak interaction of the chlorine trifluoride with the solid product. Analysis of the solid reaction product after pumping (2.30 mmoles, 0.882 g) showed it to be ClF_3PtF_5.

When an excess of platinum hexafluoride was used in the system, the reaction again proceeded as expected. To determine whether a secondary reaction involving chlorine pentafluoride occurred, a

---

[1] N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 619 (1964).

[2] N. Bartlett and D. H. Lohmann, *ibid.*, 5253 (1962).

[3] B. Weinstock, J. G. Malm, and E. E. Weaver, *J. Am. Chem. Soc.*, **83**, 4310 (1961).

[4] F. P. Gortsema and R. H. Toeniskoetter, *Inorg. Chem.*, **5**, 1217 (1966).

[5] J. R. Froning, M. K. Richards, T. W. Strickling, and S. G. Turnbull, *Ind. Eng. Chem.*, **39**, 275 (1947).

[6] K. K. Kelley, U. S. Bureau of Mines Bulletin 383, Government Printing Office, Washington, D. C., 1935.

[7] O. Ruff and H. Kurg, *Z. Anorg. Allgem. Chem.*, **190**, 270 (1930).

[8] O. Ruff and W. Menzel, *ibid.*, **202**, 49 (1931).

[9] H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, **28**, 285 (1958).

[10] H. Haendler, S. W. Bukata, B. Millard, E. I. Goodman, and J. Littman, *ibid.*, **22**, 1939 (1954).

[11] J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 1877 (1963).

[12] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 1965).

TABLE I

STOICHIOMETRIC DATA

A	B	C	D	E	C/B	D/B	E/B	No. of runs
$^3/_2ClF_3$ +	PtF_6 →	ClF_3PtF_5	+ $^1/_2ClF_5$		0.97 ± 0.02	0.50 ± 0.04		7
	ClF_3PtF_5 →	PtF_4	+ ClF_3	+ $^1/_2F_2$	1.07 ± 0.04	1.04 ± 0.04	0.44 ± 0.10	4
$^3/_4N_2F_4$ +	PtF_6 →	$PtF_{4.5}$	+ $^3/_2NF_3$		1.03 ± 0.02	1.53 ± 0.07		9
$^1/_2N_2F_4$ +	PtF_6 →	PtF_5	+ NF_3		1.00 ± 0.10	0.92 ± 0.1		2

mixture of platinum hexafluoride (3.07 mmoles, 0.945 g) and chlorine pentafluoride (2.58 mmoles) was held in a nickel reactor at 25° for 12 hr. Analysis of the product gases indicated that most of the chlorine pentafluoride (61%) and platinum hexafluoride (78%) was unchanged. A small amount (0.257 g) of yellow solid recovered was shown by chemical analysis to be ClF_3PtF_5. Decomposition of chlorine pentafluoride into fluorine and chlorine trifluoride and subsequent reaction of the chlorine trifluoride with platinum hexafluoride appeared to be the source of the ClF_3PtF_5.

Thermal Decomposition of ClF_3PtF_5.—A weighed sample of the compound (2.48 mmoles, 0.950 g) was placed in a nickel tube and, after evacuation, was heated slowly to 500°. Decomposition of the solid with evolution of gas began at 100° and appeared to be complete at 500°. The product gases were separated by trap to trap distillation and were analyzed by vapor pressure and infrared measurements. They consisted of 1.24 mmoles of fluorine (identified by reaction with fresh mercury)[13] and 2.59 mmoles of chlorine trifluoride. The brown solid, 0.7036 g (2.59 mmoles), was shown by chemical analysis and the X-ray diffraction pattern[1] to be platinum tetrafluoride.

Anal. Calcd for PtF_4: Pt, 72.0; F, 28.0. Found: Pt, 71.1; F, 28.8. The density of the platinum tetrafluoride was found to be 6.80 ± 0.23 g/cc, which compares favorably with the calculated value of 7.10 g/cc.[1]

Reaction of Platinum Hexafluoride with Bromine Pentafluoride.—Platinum hexafluoride (3.43 mmoles, 1.060 g) and bromine pentafluoride (3.43 mmoles) were condensed at −196° into a nickel reactor. The mixture was then heated at 100° for 72 hr. The volatile products were bromine pentafluoride (1.62 mmoles) and an unmeasured quantity of fluorine. A small quantity of bromine trifluoride was also obtained. The nonvolatile residue (1.163 g) was a black viscous liquid.

Anal. Calcd for $BrPt_2F_{14}$: Pt, 53.0; F, 36.1; Br, 10.9. Found: Pt, 53.4; F, 37.2; Br, 11.5.

The black liquid at 25° very slowly evolved bromine pentafluoride. With continued pumping at 10^{-4} mm, an additional 1.52 mmoles of bromine pentafluoride was obtained for a final recovery of 91.6%. The residue after pumping on the liquid was a red-brown solid. When the reaction was repeated in fluorine at 11 atm, the product again was the black viscous liquid.

Reaction of Platinum Hexafluoride with Tetrafluorohydrazine.—Platinum hexafluoride (3.50 mmoles, 1.081 g) and tetrafluorohydrazine (7.45 mmoles) were condensed into a nickel reactor at −196°, warmed to 25° over a period of 30 hr, and then heated at 70° for 24 hr. The gaseous reaction mixture, 9.95 mmoles, consisted of nitrogen trifluoride and tetrafluorohydrazine. Chromatographic analysis of the gas indicated 50.4% nitrogen trifluoride. The residue, 0.998 g, was a red-brown, very hygroscopic solid with a density of 5.28 g/cc.

Anal. Calcd for $PtF_{4.5}$: Pt, 69.5; F, 30.5. Found: Pt, 68.7; F, 28.7.

The infrared spectrum of the solid in Nujol mull gave bands at 670 (sh) 650, 620 (sh), and 560 cm^{-1}.

In another experiment, a mixture of 3.26 mmoles of platinum hexafluoride and 1.63 mmoles of tetrafluorohydrazine was warmed slowly from −196 to 25° over a period of 24 hr, followed by heating at 70° for 5 days. The solid product was 2.95 mmoles of a dark red, extremely hygroscopic solid which was shown by its melting point (80–85°) and its disproportionation behavior upon heating to be platinum pentafluoride. The gaseous product, 2.72 mmoles, was identified from its infrared spectrum as nitrogen trifluoride. No unchanged tetrafluorohydrazine was present.

Results and Discussion

The stoichiometric data given in Table I, together with the chemical analyses of the solid product, indicate that the reaction between chlorine trifluoride and platinum hexafluoride can be described by the equation

$$3ClF_3 + 2PtF_6 \longrightarrow 2ClF_3PtF_5 + ClF_5 \qquad (1)$$

Because this reaction is quantitative at 25° and nearly complete at −78°, no evidence for an intermediate complex ClF_3PtF_6 was obtained.

Decomposition of the compound ClF_3PtF_5 at temperatures to 500° took place according to the equation

$$ClF_3PtF_5 \longrightarrow PtF_4 + ClF_3 + {}^1/_2F_2 \qquad (2)$$

When the decomposition was carried out in fluorine at temperatures to 350°, the major gaseous product was chlorine trifluoride. A small amount of chlorine pentafluoride and, in some cases, chlorine monofluoride was obtained. However, no platinum hexafluoride was formed. The decomposition reaction in a fluorine atmosphere did not appear to go to completion and the solid residue consisted of a mixture of platinum tetrafluoride and ClF_3PtF_5.

Bartlett and Lohmann have speculated on the structure of ClF_3PtF_5 and suggested either a bifluorine-bridged monomer or a monofluorine-bridged polymer.[1] Infrared evidence points to the possibility of its existence as the salt $ClF_2^+PtF_6^-$. The spectrum consists of a strong band at 561 cm^{-1} with two shoulders at 529 and 505 cm^{-1}. The bands at 529 and 505 cm^{-1} are close to the symmetric and asymmetric stretching frequencies reported for the difluorochlorinium ion in the compounds $ClF_2^+AsF_6^-$ (519 and 558 cm^{-1}) and $ClF_2^+BF_4^-$ (518 and 536 cm^{-1}).[14] The absorption at 561 cm^{-1} is very close to that found for the PtF_6^- ion in the compounds O_2PtF_6, $NOPtF_6$, and NO_2PtF_6.[4] Hence these assignments of the infrared bands are consistent with the ionic structure ClF_2^+-PtF_6^-.

Platinum hexafluoride is unable to oxidize bromine pentafluoride to a higher valence state under the conditions studied (100°). However, some reaction does occur, the products being fluorine and a black, viscous liquid of approximate composition $BrPt_2F_{14}$. With continued pumping at 10^{-4} mm, the black liquid slowly evolved bromine pentafluoride and possibly some bromine trifluoride. Eventually this treatment

---

[13] R. E. Seaver, "Analysis of Fluorine Gas by Reaction with Mercury," NASA TN D-1412, Aug 1962.

[14] K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).

converted the liquid into a red-brown solid, the composition of which was close to that of platinum tetrafluoride, but still containing small amounts of bromine.

Whether the black liquid represents a reaction product or not is difficult to ascertain. It may be that at 100°, the principal reaction is the thermal decomposition of platinum hexafluoride and the black liquid which forms is a solution of platinum tetrafluoride and platinum pentafluoride in bromine pentafluoride. This suggestion would accord with the findings of Weinstock, *et al.*,[3] that, although a black liquid forms, the stoichiometry of the reaction between platinum hexafluoride and bromine trifluoride corresponds only to fluorination to bromine pentafluoride.

The reaction of platinum hexafluoride with tetrafluorohydrazine gives nitrogen trifluoride and a reduced platinum fluoride. Stoichiometric measurements and chemical analyses of the solid products indicate that the reaction takes place in stepwise fashion according to the equations

$$2PtF_6 + N_2F_4 \longrightarrow 2PtF_5 + 2NF_3 \qquad (3)$$

$$2PtF_5 + N_2F_4 \longrightarrow 2PtF_4 + 2NF_3 \qquad (4)$$

When an excess of platinum hexafluoride was employed, the solid product was found to have a composition close to platinum pentafluoride as required by eq 3. Moreover, the melting point (80°) was near that reported for platinum pentafluoride by Bartlett and Lohmann.[1] When an equimolar mixture of platinum hexafluoride and tetrafluorohydrazine was used, the solid was of variable composition and appeared to be a mixture of platinum tetrafluoride and platinum pentafluoride, corresponding approximately to the composition $PtF_{4.5}$. The over-all stoichiometry was

$$2PtF_6 + {}^3/_2N_2F_4 \longrightarrow 2PtF_{4.5} + 3NF_3 \qquad (5)$$

The X-ray diffraction pattern of the solid did not show the pattern for platinum tetrafluoride.[1] It is thought that the $PtF_{4.5}$ may be a solid solution of platinum tetrafluoride and platinum pentafluoride. That such solid solutions can form has been noted previously by Bartlett and Lohmann.[1] When the reaction was carried out in a large excess of tetrafluorohydrazine, reduction to platinum tetrafluoride was not complete but compositions near to it ($PtF_{4.1}$ to $PtF_{4.3}$) were produced.

Acknowledgment.—The authors acknowledge the technical assistance provided by H. V. Rothman and thank Dr. R. Didchenko for helpful discussions during the initial phases of this work. Research reported in this publication was supported by the Advanced Research Projects Agency through the U. S. Army Research Office—Durham.

Contribution from the Department of Chemistry,
University of New Hampshire, Durham, New Hampshire 03824

The Thermal Decomposition of Ammonium Hexafluoroferrate(III) and Ammonium Hexafluoroaluminate. A New Crystalline Form of Aluminum Fluoride[1,2]

By Dennis B. Shinn, David S. Crocket, and Helmut M. Haendler[3]

Received June 18, 1966

Ammonium hexafluoroferrate(III), $(NH_4)_3FeF_6$, and ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$, decompose on heating with an initial loss of 2 moles of ammonium fluoride, forming ammonium tetrafluoroferrate(III), NH_4FeF_4 (at *ca.* 140°), and ammonium tetrafluoroaluminate, NH_4AlF_4 (at *ca.* 170°). Further heating results in the gradual loss of ammonium fluoride, the final products being iron(III) fluoride mixed with oxide (at *ca.* 285°) and γ-aluminum fluoride, a new crystalline form (at *ca.* 300°). The structural relationships of the compounds are discussed. The intermediate, ammonium tetrafluoroferrate(III), was found to be tetragonal, $a = 3.78$, $c = 6.36$ A. It can also be prepared by direct reaction of iron(III) fluoride and ammonium fluoride at 180°.

Introduction

Many years ago, Poulenc[4] observed the formation of iron(III) fluoride when "ammonium iron fluoride" was heated carefully in a stream of inert gas. Thilo[5] has reported that heating ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$, below 350° results in the formation of ammonium tetrafluoroaluminate, NH_4AlF_4, which at higher temperatures decomposes to aluminum fluoride. Thakur, Rock, and Pepinsky[6] studied the thermal behavior of aluminum fluoride, as did Roy,[7] but concluded that further investigation was needed.

The two hexafluoro compounds have been known for a long time, but much of the early work was put in doubt by the observations of Cox and Sharpe,[8] who

---

(1) Taken in part from the M.S. thesis of D. B. Shinn.

(2) Supported in part by the U. S. Atomic Energy Commission.

(3) To whom communications should be addressed.

(4) C. Poulenc, *Compt. Rend.*, **115**, 941 (1892).

(5) E. Thilo, *Naturwissenschaften*, **26**, 529 (1938).

(6) R. L. Thakur, E. J. Rock, and R. Pepinsky, *Am. Mineralogist*, **37**, 695 (1952).

(7) R. Roy, *J. Am. Ceram. Soc.*, **37**, 581 (1954).

(8) B. Cox and A. G. Sharpe, *J. Chem. Soc.*, 1798 (1954).