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Reaction of Platinum Hexafluoride with Chlorine Pentafluoride

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Received June 30, 1968

Introduction

Reactions of platinum hexafluoride with other oxidizing agents have been studied by several investigators.[1-6] With chlorine trifluoride, difluorochloronium(III) hexafluoroplatinate(V) (ClF_2PtF_6), and chlorine pentafluoride[7] are produced.[6] Gortsema and Toeniskoetter[6] also attempted to react platinum hexafluoride with chlorine pentafluoride; the only product observed, in addition to the reactants, was a yellow solid believed to be ClF_2PtF_6 (it was assumed that it resulted from the decomposition of chlorine pentafluoride into chlorine trifluoride and fluorine and subsequent reaction of chlorine trifluoride with platinum hexafluoride).

We have recently reinvestigated the reactions of platinum hexafluoride with chlorine trifluoride, bromine pentafluoride, and chlorine pentafluoride. In the case of reactions with the first two reactants, our results are essential agreement with previous work[6] (the differences are noted below). With chlorine pentafluoride, a solid product, believed to be tetrafluorochloronium(V) hexafluoroplatinate(V) (ClF_4PtF_6), was obtained. The cation ClF_4^+ has not been reported previously.

Experimental Section

Equipment. The vacuum system used in this work consisted of a nickel manifold constructed from 1/4″ nickel pipe to which a number of subsystems were attached. These were (1) a multipurpose line for handling, measuring, and transferring reactants, (2) a line for purifying and storing fluorine, and (3) a similar line for purifying halogen fluorides. All valves (Hoke TM 413 monel diaphragm valves with metal seats) were silver soldered to the manifold outlets. Pressure measurements were made with the Wallace and Tiernan Gauge, Model FA 145, accurate to 0.2 torr. Volumes were calibrated using pure helium and a bulb of known volume.

Ten cm^3 nickel reactors were constructed from 1/2″ O.D.×4″ tubing; one end was sealed by welding; the other end was attached to a Hoke M327A monel valve with a Swagelok fitting.

Ten cm^3 Kel-F and Teflon reactors were fabricated from 3/8″×4″ Kel-F and Teflon rods; the internal diameter was 5/16″. These reactors were also equipped with Hoke M327A monel valves.

The vacuum system and nickel reactors were passivated with fluorine at ~300° using a heat gun. Passivation was considered complete when pressure at ambient temperature was identical before and after heating to 300° Before each run, the whole system was passivated with chlorine pentafluoride followed by a final passivation with platinum hexafluoride.

Materials. Platinum hexafluoride was obtained from Ozark-Mahoning Company, Tulsa, Oklahoma. The material was further purified by low temperature distillation according to the procedure described.[1] The infrared spectrum[8] and vapor pressure of the pure material agreed well with the published values.

Chlorine pentafluoride was obtained from Rocketdyne, a division of North American Aviation, Canoga Park, California. The material was used without further purification.

Bromine pentafluoride was obtained from Matheson Company and was purified by condensing it into a monel cylinder containing potassium fluoride.[9] An infrared spectrum of the material treated in this manner showed no impurities.[10] The purified BrF_5 was transferred from the cylinder as required.

Chlorine trifluoride was obtained from the Matheson Company and was purified by forming potassium chlorotetrafluoride with potassium fluoride.[9] The volatile imprities were removed by pumping at ambient temperature. Pure chlorine trifluoride[11] was generated at 130-150° as required.

Analysis. The platinum compounds were transferred into a 50-ml. quartz reactor that had been previously weighed in the dry box and purged with dry nitrogen. The reactor was then connected to the

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

[6] F. P. Gortsema and R. H. Toeniskoetter, *Inorg. Chem.*, *5*, 1925 (1966).

[7] D. Pilipovich, *et al.*, *Inorg. Chem.*, 6, 1918 (1967).

[8] B. Weinstock, H. H. Claassen, and J. G. Malm, *J. Chem. Phys.*, *32*, 181 (1960).

[9] C. J. Schack, H. E. Dubb, and J. Quagliano, Jr., *Chem. and Ind.*, 545 (1967).

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

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

vacuum system to remove the nitrogen and re-weighed. The sample was frozen at −196° and 5-10 ml. of double-distilled water was transferred to the sample. Immediate reaction was accompanied by a flash when vapor initially came into contact with the sample. The sample was warmed to ambient temperature by removing the liquid nitrogen trap. After half an hour at ambient temperature, the solution was re-frozen to −196° and 5-10 ml. of hydrazine was transferred to it. The solution was again warmed to ambient temperature. The platinum solids formed by hydrolysis and reduction were filtered off; they were redissolved with aqua regia to convert the platinum containing materials to chloroplatinic acid. The solution was diluted with water, reduced with sodium formate,[12] and the finely divided platinum metal was filtered, dried, and weighed. After additional dilution, aliquots of the stock solution were analyzed for chlorine and fluorine. Chloride ion was determined by anodic chronopotentiometry using a silver electrode. Fluoride ion was determined potentiometrically with an Orion fluoride ion electrode.[13] The above methods were checked with standard samples.

X-ray diffraction studies were carried out using the powder techniques with samples sealed in 0.3 mm thin wall quartz capillary tubes. The tubes were previously flamed in a vacuum line to remove moisture. Samples were loaded in a dry box, flushed with dry nitrogen, sealed with Kel-F grease, and placed in 5.73 cm Debye-Sherrer camera. Measurements were made using copper $K_{\alpha 1}$ radiation with a nickel filter. Exposure times varied from half and hour to four hours. Intensities were estimated visually.

Infrared spectra were obtained with Beckman IR-5A and Perkin-Elmer 337 spectrophotometers. Gaseous spectra were obtained using a 10-cm. nickel cell equipped with silver chloride windows. The solid adducts were found to be very hygroscopic and reactive with Nujol, and small explosions occurred while attempting to prepare mulls. Potassium chloride pellets were made using a Mini-Press (Wilks Scientific Corporation). Spectra were also obtained on the material pressed between chloride windows of the nickel infrared cell.

Reaction of Platinum Hexafluoride with Chlorine Pentafluoride. (a) *Kel-F reactor.* One mmole (0.309 grams) of platinum hexafluoride, and 0.5 mmole (0.065 gram) of chlorine pentafluoride were condensed at −196° into an evacuated Kel-F reactor. The color of the solid immediately changed from orange to green, and finally to purple. When the reactor was gradually warmed to ambient temperature, a brown deposit was formed on the walls of the reactor and a yellow solid on the bottom of the reactor. When the reaction mixture was condensed and warmed again to ambient temperature, the reactor cracked. The cracking was also experienced in two other reactions between PtF_6 and ClF_5 in the Kel-F reactor.

(b) *Teflon Reactor.* In an attempt to use Teflon as the reactor material for the reaction of ClF_5 and PtF_6, 0.5 mmole (0.065 gram) of ClF_5 and 1 mmole (0.309 grams) of PtF_6 were condensed at −196° into the evacuated reactor. The reaction mixture was slowly warmed from −196° to ambient temperature over a period of 14 hours. The infrared spectra of the gaseous products after low temperature distillation were found to be due to chlorine pentafluoride and platinum hexafluoride. A reddish material appeared to be dissolved by the reactor; it was impossible to remove it from the walls. When the reactor was heated to 50°C, ClF_5 started to evolve and continued to do so for 4 hours.

It was observed in a different reactor that ClF_5 was soluble in the Teflon reactor; 24 hours at 50° were required to remove all of the ClF_5. Because of the solubility of both ClF_5 and the product formed with PtF_6 in Teflon, the use of the Teflon reactor was abandoned.

(c) *Nickel Reactor.* In a typical reaction, 2 mmoles (0.618 gram) of platinum hexafluoride and 2 mmoles (0.260 gram) of chlorine pentafluoride were condensed at −196° into an evacuated, pre-passivated nickel reactor. The reaction mixture was slowly warmed to ambient temperature. The mixture was left at 23-24° for a period of 10 days. The gaseous mixture was found to contain only ClF_5 (0.10 mmoles) and F_2 (0.5 mmole). The solid had a vapor pressure of 2 torr at 23°. It appeared to be decomposing at this temperature to give ClF_5 and F_2. The reddish solid was analyzed according to the procedure described.

Anal. Calcd. for ClF_4PtF_6: Pt, 46.4; F, 45.2; Cl, 8.34. Found: Pt, 45.6; F, 44.82; Cl, 7.40.

When the reddish solid was hydrolyzed with water by transferring the water to the sample maintained at −196°, there was a flash when the water vapor initially came into contact with the solid. The reaction mixture was slowly warmed to ambient temperature. A vigorous reaction took place, and the solution turned black. The volatile material that was formed was identified as $FClO_3$ from its infrared spectrum.[14] The analysis of the solution showed no chlorine, 45.6 per cent platinum and 36.9 per cent fluorine. Chlorate or chloride are present in solution if the hydrolysis is sufficiently slow. When the sample was reduced with hydrazine after the hydrolysis, no $FClO_3$ was observed, indicating that perchloryl fluoride reacted with hydrazine completely.

The solid ignited when ground in Nujol and flashed with water resulting in a sharp explosion. It attacked NaCl plates, generating smoke. In one case, the material exploded when mixed with Nujol. A KCl pellet was prepared for infrared analysis using a Mini-Press (Wilks Scientific Corporation). The solid appeared to decompose; the spectrum showed strong bands at 470, 580 and 730 cm^{-1}.

The infrared spectrum of the material pressed between silver chloride plates is described in the Discussion Section. The X-ray powder pattern of the solid is given in Table I.

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[13] M. S. Frant and J. W. Ross, Jr., *Science, 154*, 1553 (1966).

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Table I. X-ray powder diffraction pattern of ClF_4PtF_6

d(obsd.)	Intensity [a]	$Q_{obs.}=1/d^2$	$Q_{calc.}$	hkl
6.21	W	0.0259	0.0263	101
5.81	M	0.0296	0.0299	110
4.66	W	0.0460	0.0454	002
4.09	S	0.0598	0.0592	200
3.90	MS	0.0657	0.0644	111
3.38	W broad	0.0875	0.0861	121
3.16	W	0.1001	0.1021	003
2.92	M broad	0.1173	0.1170	103
2.50	VW broad	0.1600	0.1619	203
2.35	VW	0.1815	0.1815	004
2.19	VW	0.2083	0.2058	321
2.11	VW	0.2246	0.2218	223
2.04	W	0.2394	0.2374	400
1.93	W broad	0.2699		
1.77	W	0.3188	0.3162	304
1.70	W	0.3477	0.3435	205
1.61	W	0.3844	0.3853	501 431
1.54	W	0.4233	0.4233	106
1.44	W	0.4816	0.4792	522

[a] W=weak, M=medium, S=strong, MS=medium strong, and VW=very weak.

(d) *Thermal Decomposition of ClF_4PtF_6.* A weighed sample of the compound (1.29 mmoles, 0.544 g) was placed in a quartz reactor which had been previously passivated, evacuated, and slowly heated to 350°. Decomposition of the solid with evolution of a gas was intensified at 50°. The red material turned into a black solid. The volatile products were identified as ClF_5 and fluorine. Continued heating produced more ClF_5; at 200° the black solid turned into a black viscous liquid. At this point evolution of platinum hexafluoride (red gas) began with simultaneous emission of chlorine pentafluoride. After the evolution of gases stopped, the reactor was weighed and found to have lost 0.38 g of the initial weight. The remaining solid was analyzed and found to be platinum tetrafluoride.

Anal. Calcd. for PtF_4: Pt, 72.0; F, 28.0. Found: Pt, 71.2; F, 27.6.

Reaction of Platinum Hexafluoride with Chlorine Trifluoride. Chlorine pentafluoride and a yellow solid, ClF_2PtF_6, were obtained in agreement with Gortsema and Toeniskoetter.[6] The experimental conditions in this reaction and the reaction with bromine pentafluoride (see below) were similar to those employed in the reaction of platinum hexafluoride with chlorine pentafluoride. However, contrary to previous work,[6] the infrared spectrum of the material pressed between silver chloride plates in a nickel cell was found to consist of broad bands at 800 (shoulder), 765, 645, and 630 cm^{-1}.

Reaction of Platinum Hexafluoride with Bromine Pentafluoride. The products, using a 1:1 mole ratio of PtF_6 to BrF_5, consisted of fluorine, bromine pentafluoride, and a non-volatile dark viscous liquid of the composition $BrF_4Pt_2F_{10}$, in agreement with previous work.[6] The use of a 1:3 mole ratio of PtF_6 to BrF_5 resulted in a volatile product at 50°; this material was not characterized.

Results and Discussion

The solid product obtained in the reaction between platinum hexafluoride and chlorine pentafluoride is believed to be ClF_4PtF_6, in accordance with the equation

$$ClF_5+PtF_6 \rightarrow ClF_4PtF_6+1/2F_2 \qquad (1)$$

The reaction proceeds essentially to completion as indicated by the mole ratio of 0.95 of ClF_4PtF_6 to platinum hexafluoride. The solid appears to be stable in the dry box, but decomposes slowly at room temperature under vacuum. The decomposition at elevated temperatures results in chlorine pentafluoride, platinum hexafluoride and platinum tetrafluoride; the following reactions are indicated

$$ClF_4PtF_6 \xrightarrow{\Delta} ClF_5+PtF_5 \qquad (2)$$

$$2PtF_5 \xrightarrow{\Delta} PtF_6+PtF_4 \qquad (3)$$

Although platinum pentafluoride was not observed, it is known to disproportionate readily[3] at elevated temperatures.

The X-ray powder pattern for ClF_4PtF_6 (Table I) was indexed in the tetragonal system by trial and error. From this data, the estimated unit cell dimensions are $a_0=8.176$ Å and $c_0=9.388$ Å. The volume of the unit cell calculated to be 628 Å^3. Using the method described by Zachariasen,[15,16] and recently applied by Penneman[17] (neglecting the volume contribution of the chlorine and platinum atoms), the volume for $KPtF_6$ or O_2PtF_6[2] is approximately 120 Å^3; if the volume of the potassium[17] (21 Å^3) or the dioxygenyl[2] ion (23 Å^3) is subtracted from the total volume, the volume of PtF_6^- ion is approximately 98 Å^3. Therefore, the volume of the individual fluorine atom is approximately 16.2 Å^3. Hence the number of fluorine atoms per unit cell in the compound must be the volume of the unit cell divided by the volume of the fluorine atom which is 38.8 or roughly 40. If the number of molecules in the unit cell is 4 (very common for the tetragonal system),[18] then each molecule must contain ten fluorine atoms. The average volume of the fluorine atom thus obtained for ClF_4PtF_6 (15.7 Å^3) is in fair agreement with that calculated for O_2PtF_6 (16 Å^3) and $KPtF_6$ (16.3 Å^3). The slight decrease in volume is not readily explained, especially since the volume of the chlorine atom was ignored. This result, however, is still within range of the average volume of fluorine atoms as discussed by Penneman.[17]

The infrared spectrum of solid ClF_4PtF_6 pressed between silver chloride plates consists of bands at 795, 770 (broad), 730 (shoulder), and 650 cm^{-1}. The spectrum of the solid condensed on AgCl windows consist

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of bands at 810 (shoulder), 770, 730, and 655 cm^{-1}. The last band may be attributed to PtF_6^- ion;[4] the other bands may be attributed to the Cl–F stretching modes on the basis of comparison to other chlorine-fluorine species, such as ClF_2^+,[19] ClF,[20] ClF_3,[11] and ClF_5.[10] The presence of ClF_2^+ and adsorbed ClF_5 in the sample cannot be excluded. Assignment of infrared frequencies on the basis of a given symmetry is premature; it should be noted, however, that ClF_4^+ is isoelectronic with SF_4 (C_{2v} symmetry).[21]

The ClF_4PtF_6 spectrum in a KCl pellet contained a band at 580 cm^{-1} which may be attributed to the PtF_6^{2-} ion;[4] this may be taken as an indication that the material reacted with KCl (or the moisture adsorbed on KCl).

Acknowledgment. The authors wish to express their appreciation to Dr. Charles Bock and Capt. Mark Hudgson for their help with the interpretation of the X-ray diffraction powder patterns and to Mr. John Leahy for the analyses of these reactive and sometimes explosive componds.

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