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The Systems Xenon Hexafluoride–Arsenic Pentafluoride and Xenon Hexafluoride–Phosphorus Pentafluoride

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The reaction of XeF_6 with AsF_5 was reported by Selig to yield the compound $XeF_6 \cdot AsF_5$.[1] Since three complex compounds, $2XeF_6 \cdot SbF_5$, $XeF_6 \cdot SbF_5$, and $XeF_6 \cdot 2SbF_5$, exist in the XeF_6–SbF_5 system,[2] it was thought that by varying the proportions of the reactants more than one complex compound might be isolated in the XeF_6–AsF_5 system. Such was found to be the case. The compound $2XeF_6 \cdot AsF_5$ was readily prepared by the reaction of excess XeF_6 with AsF_5. The reaction of excess AsF_5 with XeF_6, however, yielded only $XeF_6 \cdot AsF_5$.

The 2:1 compound is a white, crystalline solid which hydrolyzes violently to give a nearly quantitative yield of Xe(VI) in solution. When pumped at room temperature, $2XeF_6 \cdot AsF_5$ loses XeF_6 very slowly and eventually forms $XeF_6 \cdot AsF_5$.

The reaction between XeF_6 and PF_5 occurred readily to form the white solid $2XeF_6 \cdot PF_5$. This compound was prepared by allowing either XeF_6 or PF_5 to be in excess. It is surprising that no evidence was obtained for the existence of any other complex compounds in this system. The compound was found to have a dissociation pressure of about 9 mm at room temperature. When pumped at 0°, XeF_6 and PF_5 were removed in a 2:1 molar ratio. The substance hydrolyzed violently to give a nearly quantitative yield of Xe(VI) in solution.

Experimental Section

Reagents.—Xenon hexafluoride was prepared by the combination of the elements under pressure at about 225°. Arsenic pentafluoride (98% purity) and phosphorus pentafluoride (99.5% purity) were obtained from Research Inorganic Chemicals, Inc. and were used directly from the cylinders. A second source of PF_5 was the reaction of PF_3 with F_2. The PF_5 obtained from this reaction was purified by low-temperature vacuum distillation. Infrared spectral analysis showed the reagents to be essentially pure. Only traces of common impurities such as SiF_4, $XeOF_4$, and POF_3 were detected.

Equipment.—Prefluorinated Monel and stainless steel reactors equipped with brass Hoke valves were used for the reactions. The reactors could be opened to allow solid adducts to be removed for study. The XeF_6 was handled in a prefluorinated metal vacuum line.

Preparation and Decomposition of $2XeF_6 \cdot AsF_5$.—In a typical experiment 0.7122 g (2.90 mmoles) of XeF_6 was distilled into a reactor containing 0.1939 g (1.14 mmoles) of AsF_5 (molar ratio, 2.54:1). The reactants were contacted at room temperature for 18 hr. The mixture was then pumped at room tempeature, and the weight decreased as shown in Figure 1. The material removed by pumping was collected in a trap at −196° and at intervals was removed and analyzed for xenon. Unreacted XeF_6 (calcd for XeF_6: Xe, 53.5; found: Xe, 53.6) was rapidly removed by pumping to leave $2XeF_6 \cdot AsF_5$ followed by further slow loss of XeF_6 (found: Xe, 53.1, 52.0) to yield eventually $XeF_6 \cdot AsF_5$ (calcd for $XeF_6 \cdot AsF_5$: Xe, 31.6; found: Xe, 31.7).

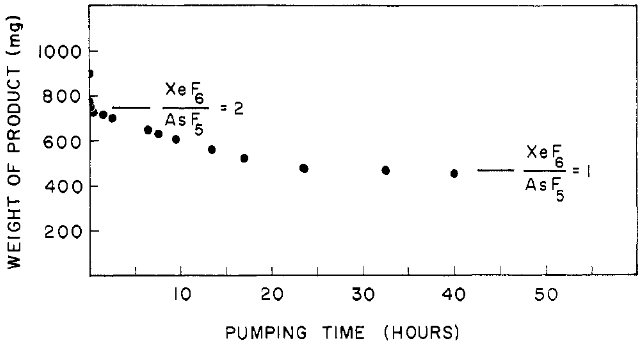

Figure 1.—Illustration of the preparation and subsequent decomposition under vacuum of $2XeF_6 \cdot AsF_5$.

Properties of $2XeF_6 \cdot AsF_5$.—The complex was a white, crystalline solid which was very hygroscopic and attacked dry glass only slowly. It reacted violently with water, but only a little O_2 (0.7 equiv/mole of $2XeF_6 \cdot AsF_5$) was detected as a product of reaction. The addition of a solution of KI to the hydrolyzed material resulted in the formation of large quantities of I_2 and Xe. Titration of the I_2 with sodium thiosulfate indicated a liberation of 11.5 equiv of I_2/mole of $2SeF_6 \cdot AsF_5$. (Total oxidizing equivalents found: $11.5 + 0.7 = 12.2$; theoretical : 12.0.)

When samples of $2XeF_6 \cdot AsF_5$ were sealed in glass tubes under an atmosphere of dry nitrogen and heated to about 110°, a pale yellow vapor (presumably XeF_6) could be seen above the solid. The color became more intense as the temperature was raised. At about 125° most of the solid melted to a viscous liquid. Melting occurred over a range of temperature and a little solid remained even at 132°. The liquid froze on cooling. The solid probably melted over a wide range because of the presence of impurities formed from attack on the glass under these conditions. One of the properties observed in this research for $XeF_6 \cdot AsF_5$, however, was that it melted at 130.5°. Since samples of $2XeF_6 \cdot AsF_5$ dissociated into XeF_6 and $XeF_6 \cdot AsF_5$ on heating, it is possible that the molten material formed when $2XeF_6 \cdot AsF_5$ was heated to 125° was largely $XeF_6 \cdot AsF_5$.

Reaction of Excess AsF_5 with XeF_6.—Several reactions were run on a millimole scale under various conditions. Molar ratios of AsF_5 to XeF_6 as high as 10:1 were used. Temperatures of reaction ranged from 22 to 90°. In spite of the many reactions run, no complex compound other than $XeF_6 \cdot AsF_5$ was observed. Apparently the hypothetical compound $XeF_6 \cdot 2AsF_5$, analogous to $XeF_6 \cdot 2SbF_5$,[2] does not exist.

X-Ray Powder Patterns.—X-Ray powder photographs were taken of samples of both $2XeF_6 \cdot AsF_5$ and $XeF_6 \cdot AsF_5$. The compounds were handled as previously described.[3] The powder patterns obtained were distinctly different from one another.[4]

Preparation and Decomposition of $2XeF_6 \cdot PF_5$.—The complex was prepared by allowing either XeF_6 or PF_5 to be in excess. Using PF_5 in excess had the advantage that the unreacted PF_5 could be pumped away at a temperature at which XeF_6 is essentially nonvolatile (such as −78°). When XeF_6 was used in excess, the process of pumping removed some PF_5 along with XeF_6. This resulted from the fact that the dissociation pressure of $2XeF_6 \cdot PF_5$ at a given temperature is a substantial fraction of the vapor pressure of XeF_6.

In a typical experiment involving excess PF_5, 0.2876 g (1.17 mmoles) of XeF_6 was contacted with 0.2713 g (2.15 mmoles) of PF_5 (molar ratio, 1:1.84) for 24 hr at 22°, 12 hr at 0°, and 2 hr at −11°. The unreacted PF_5 was then removed by pumping at −78° for 5 min. The weight of the product remaining in the

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(1) H. Selig, *Science*, **144**, 537 (1964).

(2) G. L. Gard and G. H. Cady, *Inorg. Chem.*, **3**, 1745 (1964).

(3) K. E. Pullen and G. H. Cady, *Inorg. Chem.*, **5**, 2057 (1966).

(4) K. E. Pullen, Ph.D. Thesis, University of Washington, 1967.

reactor, 0.3628 g, corresponded to a composition of 1.94$XeF_6 \cdot PF_5$. The substance in the reactor was then removed by pumping at 0°. The complex could be pumped away at that temperature at a rate of about 10 mg/min in the system employed. Analysis of the sublimate for Xe at two random intervals indicated that XeF_6 and PF_5 were being lost close to a 2:1 molar ratio (calcd: Xe, 42.7; found: Xe, 43.0, 41.0).

In a typical experiment involving excess XeF_6, 0.3255 g (1.32 mmoles) of XeF_6 was contacted with 0.0653 g (0.518 mmole) of PF_5 (molar ratio, 2.54:1) for 24 hr at 22° and 3 hr at 0°. The mixture was then pumped at 0°. Pumping for 0.5 min produced a weight loss of 57.4 mg. The analysis for Xe (found: 49.4) corresponded to a loss of 53.0 mg of XeF_6 and 4.4 mg of PF_5. Pumping for another minute resulted in a further weight loss of 40.4 mg. The analysis for Xe (found: 48.8) corresponded to a loss of 36.8 mg of XeF_6 and 3.6 mg of PF_5. The XeF_6 to PF_5 molar ratio of the material remaining in the reactor at this point was 2.08:1. The pumping was then continued, but additional weight was lost at a slower average rate (about 11 mg/min). Analysis of the sublimate for Xe at three random intervals indicated that the rest of the material was pumped away with a molar ratio of XeF_6 to PF_5 close to 2.0 (found: Xe, 43.9, 43.3, 42.0).

Properties of $2XeF_6 \cdot PF_5$.—The dissociation pressure of the complex was measured using an apparatus which consisted of a glass manifold and a prefluorinated copper manifold, each having a volume of about 30 cm^3. The two manifolds were connected and could be closed off from each other by means of a metal valve. The glass manifold was equipped with a mercury manometer.

With the valve separating the two manifolds open, the reaction vessel containing the complex was attached to the metal manifold and both manifolds were evacuated. The valve connecting the two manifolds was then closed and the valve of the reaction vessel was opened. The glass manifold was filled with dry nitrogen to a pressure estimated to be equal to the dissociation pressure of $2XeF_6 \cdot PF_5$ at the temperature in question. After equilibrium in the metal portion of the system had been reached, the valve of the reactor was closed, the valve separating the manifolds was opened, and the change in pressure was noted. The gases were then pumped out, and the process was repeated (using a more suitable nitrogen pressure) until the manometer indicated no change in pressure upon opening the valve between the two manifolds. Measurements yielded the data: 8.9 mm, 23.1°; 4.8 mm, 17.7°; 2.9 mm, 12.9°; and 1.3 mm, 9.0°.

The white solid reacted violently when flooded with water, and a little O_2 (0.4 equiv/mole of $2XeF_6 \cdot PF_5$) was observed as a product of reaction. The solution remaining contained an oxidizing agent capable of liberating iodine in the proportion 11.4 equiv/mole of $2XeF_6 \cdot PF_5$ consumed (total oxidizing equivalents found: 11.4 + 0.4 = 11.8; theoretical: 12.0).

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The Formation Constant and Aquation Rate of the Nitratopentaaquochromium(III) Ion[1]

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We wish to report the results of an investigation of the formation constant and aquation rate of the nitratopentaaquochromium(III) ion. The aquation of this ion also formed the subject of a paper which appeared after this work had been completed.[3] Our kinetic data are in good agreement with the results obtained in the earlier work. We obtained, in addition, equilibrium data pertaining to the stability of the nitrato complex.

Experimental Section

Preparation of the Nitratopentaaquochromium(III) Ion.—A saturated solution of $Cr(NO_3)_3 \cdot 9H_2O$, acidified by a few drops of concentrated nitric acid, was boiled for about 20 min and then diluted tenfold with cold water. The resulting solution was passed through a cooled Dowex 50W-X8 cation-exchange resin in the H^+ form and the nitratopentaaquochromium(III) ion was eluted with 1 *M* perchloric acid. In common with Swaddle, we find that $(H_2O)_5CrNO_3^{2+}$ is also produced in good yield in the reaction of nitratopentaamminecobalt(III) with chromium(II). The nitratopentaaquochromium(III) complex has two maxima in the visible region of the spectrum, at 412 mμ (18.9) and at 581 mμ (16.1).[4] The molar absorptivities reported by Swaddle are slightly lower and the maxima are shifted toward shorter wavelengths [409 mμ (18.57) and 577 mμ (15.84)].

Equilibrium Measurements.—Solutions for the equilibrium measurements were prepared from mixtures of $Cr(NO_3)_3 \cdot 9H_2O$, perchloric acid, and nitric acid so that the final ionic strength was 1.0 *M* and the hydrogen ion concentration was 0.40 *M*. After warming the solutions for several hours at 45° they were kept for 8 half-lives of the aquation reaction at each temperature. Aliquots were then diluted tenfold with cold water and passed through a cooled Dowex 50W-X8 cation-exchange resin in the H^+ form. The nitrato complex was eluted with 1 *M* perchloric acid and hexaaquochromium(III) was eluted with 4 *M* perchloric acid. The chromium content of the fractions was determined at 327 mμ after oxidation to chromate with alkaline hydrogen peroxide. At least two samples were taken from each solution and the agreement was always better than 1%.

Kinetic Measurements.—For the kinetic measurements solutions containing the nitrato complex were passed through the Dowex resin in the Li^+ form and the complex was eluted with 1 *M* lithium perchlorate. The progress of the reaction was followed at 260 mμ on a Cary 14 spectrophotometer equipped with 10-cm cells. Plots of $\log (A_t - A_\infty)$ against t, where A_t is the absorbance of the solution at time t, gave straight lines from which the rate constants were calculated.

Results and Discussion

Equilibrium Measurements.—Values of the equilibrium constant $K = (CrNO_3^{2+})/(Cr^{3+})(NO_3^-)$ are presented in Table I. These values were calculated on the assumption that ion-pairing effects are negligible. It is apparent from Table I that there is a definite decrease in the values of the equilibrium constants with increasing nitrate concentration. This decrease in the equilibrium constant could be due either to a medium effect or to ion pairing or to both. If it is attributed solely to ion pairing (with a resulting decrease in free chromic and nitrate concentrations) and a formation constant of 0.3 M^{-1} is assumed for the ion pair, then the values become independent of the nitrate concentration at each temperature. The corrected values of K are 1.23 × 10^{-2}, 0.97 × 10^{-2}, and 0.67 × 10^{-2} M^{-1} at 34.9, 25.1, and 10.2°, respectively. The enthalpy and entropy change calculated from the corrected values are

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Visiting chemist from the Hebrew University, Jerusalem.

[3] T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

[4] The numbers in parentheses are the values of the molar absorptivities at the absorption maxima.