exchange selectivities of alkali ions as due to "a balance between (1) Coulomb interactions between the mobile counterions (in various states of hydration) and the fixed groups of the exchanger, and (2) ion-dipole and ion-induced dipole interactions between the counterions and water molecules (ionic hydration)," also lends support to our postulate discussed above regarding the ion-exchange equilibria on both types of exchangers in aqueous and mixed solvents.

As observed in the case of a strong-acid exchanger,[2] the contact type of ion-pair formation becomes more significant from about 70% (v./v.) and above of the organic solvent content in the solution phase. Also $K^{C^+}{}_{NH_4^+}$ in the presence of acetone is lower than in 2-propanol, even though the dielectric constants and the number of carbon atoms in both solvents are nearly the same.

From Table I it can be seen that the position of NH_4^+ among Li^+, Na^+, and K^+ in the presence and absence of various organic solvents is changing. This anomalous behavior may be due to its nonspherical nature as stated earlier.[2]

Similar reversal of affinities of alkaline earths as well as rare earth cations toward the two types of exchangers has been observed. The effect of organic solvents on these systems is under investigation.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Reactions of Xenon Hexafluoride with Antimony Pentafluoride, Hydrogen Chloride, Ammonia, and Perfluorocyclopentene

BY GARY L. GARD AND GEORGE H. CADY

Received July 22, 1964

By varying the proportions of the reactants antimony pentafluoride and xenon hexafluoride, it is possible to prepare each of the crystalline solids: $XeF_6 \cdot 2SbF_5$, $XeF_6 \cdot SbF_5$, $SbF_5 \cdot 2XeF_6$. Hydrogen chloride, ammonia, and perfluorocyclopentene react readily with xenon hexafluoride but the products have not been found to include substances in which xenon is in combination with chlorine, nitrogen, and carbon, respectively.

Since xenon hexafluoride reacts with water to give hydrogen fluoride and one or more compounds in which oxygen is bound to xenon,[1,2] it seems possible that reactions with certain hydrogen compounds other than water should yield hydrogen fluoride and compounds of xenon. For example, hydrogen chloride might give a chloride of xenon, or ammonia might give an amide or nitride. These two reactants have been tested but no new compounds containing xenon have been found. In each case gaseous xenon was formed. In one case, chlorine was also formed and in the other case nitrogen was a product.

An attempt was made to form an addition compound from xenon hexafluoride and an unsaturated fluorocarbon (perfluorocyclopentene). The reaction produced perfluorocyclopentane but no evidence was found for a compound containing both xenon and carbon.

Knowing that xenon hexafluoride dissolves in hydrogen fluoride to give an electrically conducting solution,[3] it was thought that the strong fluoride acceptor, antimony pentafluoride, might combine with XeF_6. It was found that the two substances combine readily, but without the evolution of much heat, and that at least three different compounds may be formed.

As the work was in progress, Edwards, Holloway, and Peacock[4] reported that either the difluoride or tetrafluoride of xenon combines with antimony pentafluoride to give $XeF_2 \cdot 2SbF_5$. It has also been learned by the authors that results similar to theirs for XeF_6 and SbF_5 have been obtained at the Argonne National Laboratory by Selig, who has already reported the formation of $XeF_6 \cdot BF_3$ and $XeF_6 \cdot AsF_5$.[5] Details of Selig's work on SbF_5 are not known to the authors.

When an excess of antimony pentafluoride reacts with xenon hexafluoride, a white solid having the composition $XeF_6 \cdot 2SbF_5$ is formed. This is soluble in liquid antimony pentafluoride, but the excess may be easily distilled away leaving the crystalline solid. When an excess of xenon hexafluoride is used, the white crystalline product remaining after vacuum distillation of the excess reagent at room temperature is $SbF_5 \cdot 2XeF_6$. If this solid is held at 50°, more xenon hexafluoride may be removed by vacuum distillation until the composition $XeF_6 \cdot SbF_5$ is reached.

X-Ray powder spectra of the three products are clearly different and are of such a nature that the $XeF_6 \cdot SbF_5$ cannot be a mixture of the other two solids. The compound $XeF_6 \cdot 2SbF_5$ melts at 108 ± 1° while neither of the other two has been observed to melt even at con-

---

(1) C. L. Chernick, H. H. Claassen, J. G. Malm, and P. L. Plurien, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 106.

(2) F. B. Dudley, G. Gard, and G. H. Cady, *Inorg. Chem.*, **2**, 228 (1963).

(3) H. H. Hyman and L. A. Quarterman, ref. 1, p. 275.

(4) A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc.*, 275 (1963).

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

siderably higher temperatures. Each of the solids sublimes under vacuum at temperatures below 100°. They react vigorously with water giving a solution containing xenon in a positive oxidation state. The reaction with potassium iodide solution gives iodine and gaseous xenon. When a sample of the one of the solids reacts with a small amount of water, a change occurs which makes the solid explosive. Probably explosive xenon trioxide is formed.

While $XeF_6 \cdot SbF_5$ and $XeF_6 \cdot 2SbF_5$ may be prepared in Pyrex glass, the use of XeF_6 results in enough attack upon glass so that metal apparatus rather than glass should be used when preparing $SbF_5 \cdot 2XeF_6$.

An X-ray structure determination for $XeF_6 \cdot 2SbF_5$ is in progress by C. H. L. Kennard.

Experimental

Preparation of Xenon Hexafluoride.—Xenon hexafluoride was prepared as described elsewhere.[2]

Materials.—Antimony pentafluoride was obtained from the Allied Chemical Co. This material was distilled and the portion boiling between 142 and 144° was used. Dry sodium fluoride was added to the distilled material and from the mixture, samples were distilled for reaction. Hydrogen chloride and ammonia were used directly from commercial cylinders.

General Methods.—Nuclear magnetic resonance spectra were obtained through the use of a Varian Model 4311B high resolution spectrometer with a 40-Mc. oscillator. Mass spectra were recorded using a Consolidated Engineering Corp. Type 21-103 mass spectrometer. X-Ray powder spectra were obtained for samples of $2XeF_6 \cdot SbF_5$, $XeF_6 \cdot SbF_5$, and $XeF_6 \cdot 2SbF_5$ contained in 0.5-mm. Lindemann glass tubes. The tubes were filled in a drybox and were sealed with a waxy polymer of chlorotrifluoroethylene. Six-hour exposures were made using a Philips powder camera which had been calibrated with a powder spectrum of sodium chloride (a = 5.63874 Å.) to give an effective radius of 57.208 ± 0.027 mm. Nickel-filtered copper radiation ($\lambda_{K\alpha}$ 1.54178 Å.) was used. Melting point determinations were made on the sublimed material in glass vessels.

Reactions of Xenon Hexafluoride. With Hydrogen Chloride.—Xenon hexafluoride (0.1624 g.) reacted with hydrogen chloride (0.147 g.) upon slowly warming from −183° to room temperature. Analysis of the products showed xenon and chlorine present in equivalent amounts. Calcd.: Xe, 0.0870 g.; Cl_2, 0.1409 g. Found: Xe, 0.0833 g.; Cl_2, 0.1353 g. Apparently, the reaction under these conditions was

$$XeF_6 + 6HCl = 3Cl_2 + 6HF + Xe$$

With Ammonia.—At room temperature ammonia was added slowly to a flask containing 0.3748 g. of xenon hexafluoride. The reaction was extremely violent. After an excess of ammonia had been added the products were found to be xenon, nitrogen, and ammonium fluoride. The reaction had proceeded as follows.

$$XeF_6 + 8NH_3 = Xe + 6NH_4F + N_2$$

With Perfluorocyclopentene.—When a mixture of xenon hexafluoride (0.2780 g.) with perfluorocyclopentene (0.2729 g.) was held at 50–70° for 2 days, most of the fluorocarbon was converted to perfluorocyclopentane, as shown by the infrared spectrum, but only a trace of free xenon was formed. One or more lower fluorides of xenon must have been produced.

Reaction of Antimony Pentafluoride in Excess with Xenon Hexafluoride to Produce $XeF_6 \cdot 2SbF_5$.—Vessels of metal or of Pyrex glass were used for this reaction. Attack upon glass by the reactants was negligible.

In one run the reactor was a small glass flask which was attached to a stainless steel valve by a metal to glass seal. The weights of reactants employed were 1.5595 g. of SbF_5 and 0.5056 g. of XeF_6 (molar ratio, 3.5:1) and the mixture was held at 75 ± 5° for 18 hr. When the vessel was then cooled to −78° only 2.8 mg. of material (largely SiF_4 with a trace of Xe as shown by a mass spectrometer) was removed by pumping. The vessel was then warmed to room temperature and the volatile material (SbF_5) was removed by pumping for 5 hr. at room temperature. A white solid product weighing 1.4013 g. remained. From the ratio of this weight to that of the XeF_6 consumed, the product was $XeF_6 \cdot 2.01SbF_5$. To make sure that no higher adduct could be formed, 7.8 g. of SbF_5 was added and the vessel was held at about 70° for 20 hr. After pumping for 8 hr. at room temperature the constant weight was 1.4276 g., corresponding to $XeF_6 \cdot 2.09SbF_5$.

The presence in the product at this stage of a small amount of yellow material which melted at about 61° suggested that a little $XeF_2 \cdot 2SbF_5$ had formed. The total weight of xenon collected in all of the volatile fractions was found by analysis to be only 8 mg.

In another run using an all-glass reactor with a stopcock lubricated with Kel-F grease a 0.1598-g. sample of XeF_6 reacted with an excess of SbF_5 at about 55° for 1 hr. to give a white solid product weighing 0.4385 g. after pumping to constant weight. This corresponded to $XeF_6 \cdot 1.95SbF_5$.

In a run made in a Monel metal reactor closed by a stainless steel valve, a 0.2445-g. sample of XeF_6 reacted with SbF_5 (1.6040 g.) at 50–60°, with a contact time of 2 hr. to give 0.7075 g. of product, after pumping to constant weight, corresponding to $XeF_6 \cdot 2.14SbF_5$. Analysis of the white solid gave 21% Xe (theoretical for $XeF_6 \cdot 2SbF_5$ is 19.4% Xe).

Reaction of Xenon Hexafluoride in Excess with Antimony Pentafluoride to Form $SbF_5 \cdot 2XeF_6$.—Since xenon hexafluoride is known to attack glass, runs involving an excess of this reagent were made in a Monel metal reactor which had been "conditioned" by treatment with fluorine and antimony pentafluoride. In one run 0.1720 g. of SbF_5 and 0.9350 g. of XeF_6 were allowed to stand together at room temperature for about 2 weeks while other studies were in progress. When the system was pumped at room temperature to substantially constant weight (total pumping time 85 min.) xenon hexafluoride but not antimony pentafluoride was removed, leaving 0.5930 g. of solid product corresponding by weight to the composition $SbF_5 \cdot 2.16XeF_6$. An additional 0.2920 g. of XeF_6 was then added and the reactor was held at 50–65° for 5 hr. The vessel was again pumped at room temperature to substantially constant weight, the same amount of product remaining as before. The material was removed from the vessel and a 0.1467-g. sample was allowed to react with an aqueous solution of potassium iodide. This vigorous reaction released 0.0541 g. of xenon corresponding to 36.9% Xe (theoretical for $SbF_5 \cdot 2XeF_6$ is 37.1% Xe).

In a second run 0.2334 g. of SbF_5 and 0.7828 g. of XeF_6 stood together for 40 hr. in the metal reactor, which had previously been "conditioned" with fluorine and antimony pentafluoride. The vessel was then pumped to substantially constant weight at room temperature, leaving 0.7787 g. of product corresponding by weight to the composition $SbF_5 \cdot 2.07XeF_6$.

Preparation of $XeF_6 \cdot SbF_5$.—After completion of the run just described, the vessel was warmed to 50° and pumping was continued with the result that xenon hexafluoride was removed rather slowly. After a pumping period of 3 hr. at 50° the loss in weight was 0.2485 g. and after an additional 4.5 hr. the total loss was 0.2695 g. Since previous work had shown that antimony pentafluoride was not removed in a case such as this, the composition of the resulting solid, from the weights involved, was $XeF_6 \cdot 1.05SbF_5$.

In another run 0.9495 g. of SbF_5 and 1.4333 g. of XeF_6 were allowed to stand together in a Monel metal vessel at room temperature for about 1 hr. The unreacted XeF_6 was then removed by pumping for 5 hr. with the vessel at room temperature. At this stage the product weighed 2.2440 g. and the molar ratio of XeF_6 to SbF_5 was 1.21:1. The vessel was then held at about 50° and pumping was continued for 7 hr. with the following results.

Time of pumping, hr.	0	2.0	3.5	5.0	7.0
Weight of product in reactor, g.	2.2440	2.0785	2.0167	1.9817	1.9732

The final weight corresponded to the composition $XeF_6 \cdot 1.05SbF_5$. Tests which were made on the material removed by pumping did not show the presence of antimony but they did show the presence of a strong oxidizing agent considered to be XeF_6.

When the reaction of an excess of XeF_6 with SbF_5 occurred in a glass vessel, a white solid was formed together with a greenish gas. There was no striking evolution of heat but the reaction gave a white cloud which settled out. Small amounts of silicon tetrafluoride and oxygen were produced. In each of two cases the solid remaining after removal of excess xenon hexafluoride had the composition $XeF_6 \cdot 1.05SbF_5$.

Properties of $XeF_6 \cdot SbF_5$.—Sublimation of a small part of the material occurred when an evacuated glass vessel containing $XeF_6 \cdot SbF_5$ was heated on the bottom to 95°. Sublimation under 1 atm. of nitrogen occurred at approximately 160°. The material reacted slowly with the hot glass producing in 3 hr. at 120° a pressure of somewhat over 10 mm. of the gases Xe, O_2, and SiF_4 (identified by mass spectrometry). When heated rather quickly in glass to 205° the substance did not melt. At approximately 114°, some of the sublimed material appeared to shrink and it fell from the heated wall.

Addition of pyridine to some $XeF_6 \cdot SbF_5$ gave a brown residue. Addition of CCl_4 produced a greenish solution and some gas (apparently chlorine) which oxidized potassium iodide to free iodine. Perfluorodimethylcyclohexane neither reacted with nor dissolved $XeF_6 \cdot SbF_5$. The substance reacted vigorously with water. It liberated iodine in a solution of potassium iodide while elementary xenon was set free.

Properties of $XeF_6 \cdot 2SbF_5$.—Sublimation under vacuum occurred readily at about 100° and was observed at temperatures as low as 55°. Very little reaction with a glass container occurred. While subliming 1.4 g. of $XeF_6 \cdot 2SbF_5$ from the bottom to the top of the vessel during a period of 5 hr. only 13.9 mg. of gases was formed, which could be removed quickly by pumping. Melting point determinations upon the sublimed material in glass and under 1 atm. of dry air gave a value of 108 ± 1° (sharp). A colorless and mobile liquid was formed.

Upon warming $XeF_6 \cdot 2SbF_5$ with a large excess of SbF_5, a yellowish solution was formed. At 70° the solid was very soluble in SbF_5. Cooling the solution to room temperature did not cause immediate crystallization; however, cooling to approximately 9° caused slow formation of large colorless crystals (probably $XeF_6 \cdot 2SbF_5$). When the solution was suddenly cooled to −183° the yellow color remained.

The ^{19}F n.m.r. spectrum at room temperature of a solution of the solid in SbF_5 gave a single broad symmetrical peak in the region for fluorine bound to antimony at a chemical shift of 32.7 p.p.m. from fluorine in trifluoroacetic acid. At room temperature, antimony pentafluoride[6] gives two broad peaks which collapse to one at about 80°. The n.m.r. spectrum of solid $XeF_6 \cdot 2SbF_5$ in the region for fluorine attached to antimony consisted of a broad asymmetrical peak which could be regarded as a peak with a shoulder. It is of interest that Peacock, *et al.*,[4] found a single peak in the antimony pentafluoride region for liquid $XeF_2 \cdot 2SbF_5$.

TABLE I

X-RAY POWDER SPECTRA

$SbF_5 \cdot 2XeF_6$		$SbF_5 \cdot XeF_6$		$XeF_6 \cdot 2SbF_5$			
d, Å.	Intensity	*d*, Å.	Intensity	*d*, Å.	Intensity	*d*, Å.	Intensity
4.64	m	5.09	m	5.06	m	1.61	l
4.44	m	4.80	m	4.69	h	1.54	l
4.25	m	4.15	h	4.26	h	1.49	l
4.04	h	3.77	m	4.12	h	1.44	l
3.84	m	3.61	m	3.85	m	1.41	l
3.70	m	3.15	m	3.68	m	1.38	l
3.10	h	2.96	l	3.59	m	1.36	m
2.64	l	2.67	l	3.41	l	1.26	l
2.49	l	2.55	l	3.19	m	1.23	l
2.34	l	2.40	l	2.93	l	1.20	l
2.26	l	2.28	l	2.80	l	1.14	l
2.05	l	2.15	l	2.42	l	1.11	l
1.97	l	2.08	m	2.33	l	1.09	l
1.95	l	1.99	l	2.27	l	1.00	l
1.79	l	1.94	l	2.08	m	0.94	l
1.69	l	1.90	l	1.99	l	0.93	l
1.66	l	1.80	m	1.95	l	0.90	l
1.62	l	1.68	m	1.92	l	0.87	l
1.55	l	1.61	l	1.83	l	0.86	l
1.42	l	1.57	l	1.80	l	0.83	l
1.32	l			1.74	l	0.80	l
1.19	l			1.70	m	0.79	l
1.16	l			1.67	l		

Properties of $SbF_5 \cdot 2XeF_6$.—Some of the solid was transferred from the Monel metal reactor to a glass vessel. It was then found to sublime under vacuum when warmed to about 65°. When the solid was stored in a glass vessel under vacuum at room temperature a slow reaction occurred giving solid $XeF_6 \cdot SbF_5$ and the gases O_2, SiF_4, and a reactive compound of xenon. Pumping at room temperature on about 0.78 g. of $2XeF_6 \cdot SbF_5$ in the Monel reactor resulted in the loss of about 4–6 mg. of XeF_6/hr. When a sample of the solid was heated to 160° rather rapidly in a glass vessel, it showed no sign of melting but the solid appeared to shrink and at about 129° it fell from the side to the bottom of the vessel.

X-Ray Powder Spectra.—Table I, which gives the X-ray powder spectra of the three compounds, lists the interplanar spacing, *d*, and the relative intensity of each measured line; h stands for high intensity, m for medium, and l for low.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research and in part with the support of a fellowship from the Allied Chemical Company. The authors thank C. H. L. Kennard for taking the X-ray spectra.

---

[6] C. J. Hoffman, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).