Normal-Coordinate Analysis. To support the above assignments for SH_3^+, a normal-coordinate analysis was carried out, the results of which are given in Table III. Since the geometry of SH_3^+ is unknown, we have computed force fields for different bond angles ranging from 90 to 110° (the bond angle in isoelectronic PH_3 is 93.345°).[25] For the bond length in SH_3^+ an estimated value of 1.33 Å was used. The force constants were computed by trial and error with the help of a computer to obtain an exact fit between observed and calculated frequencies. Three different force fields were used to show that for a vibrationally weakly coupled (heavy central atom, light ligands) species, such as SH_3^+, the choice of a particular force field is less important than other variables, such as the bond angle. To demonstrate the small variation in the computed force fields, insignificant decimals are carried in Table III. Of the three different force fields used, the diagonal force field (DFF) and the force field requiring the deformation symmetry force constants to have minimal values were selected for their established[26] usefulness for vibrationally weakly coupled species. The third force field (PH_3,TR) was computed by using the general valence force field (GVFF) off-diagonal symmetry force constants of isoelectronic PH_3 for SH_3^+. As can be seen from Table III, all three force fields yield very similar force constants. Therefore, the given force fields are likely to be good approximations of a GVFF. By comparison with the known bond angles of H_2O, CH_3^+, NH_3, H_2S, and PH_3, a bond angle of about 95° appears to be most likely for SH_3^+, although the choice of the bond angle is not very critical as can be seen from the small variation of the force constants within the most probable bond angle range of 90–100°. As expected for a vibrationally weakly coupled species containing only one stretching and one deformation vibration of very different frequency in each symmetry block, the potential energy distribution showed all fundamentals to be highly characteristic. Thus, ν_1 and ν_3 were 100% pure stretching modes and ν_2 and ν_4 were 97–99% pure deformations. Comparison of the force constants of SH_3^+ with those[23] of PH_3 shows excellent agreement thus supporting the above given assignments for SH_3^+.

Acknowledgment. The author thanks Drs. L. Grant, C. Schack, and R. Wilson for their help, Dr. E. C. Curtis for the use of his computer program for the computation of force constants, and the Office of Naval Research, Power Branch, for financial support.

Registry No. $SH_3^+SbF_6^-$, 55590-58-4; SbF_5, 7783-70-2; HF, 7664-39-3; hydrogen sulfide, 7783-06-4; $ClH_2^+SbF_6^-$, 55590-57-3.

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Hexafluoroiodine(VII) Hexafluoroantimonate(V) ($IF_6^+SbF_6^-$)[1]

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Received April 2, 1975 AIC50239I

The 1:1 complex of iodine heptafluoride and antimony pentafluoride has been prepared and has been shown to have the ionic structure $IF_6^+SbF_6^-$ by Raman and infrared spectral analysis. The X-ray powder pattern has been indexed for a cubic unit cell with $a_0 = 6.069$ Å. The complex reacts rapidly with radon gas at ambient temperature, forming a nonvolatile radon compound; hence it can be used for purification of radon-contaminated air and for analysis of radon in air. In reactions with carbon monoxide, sulfur dioxide, nitric oxide, and nitrogen dioxide, it forms COF_2, SO_2F_2, $NO^+SbF_6^-$, and $NO_2^+SbF_6^-$, respectively.

Introduction

Solid oxidants have been shown to be useful for collecting radioactive noble gases, such as ^{222}Rn and ^{133}Xe.[3–5] Among the compounds that have been used for this purpose are halogen fluoride–metal fluoride complexes, such as $ClF_2^+SbF_6^-$, $BrF_2^+BiF_6^-$, and $BrF_4^+Sb_2F_{11}^-$, the fluoronitrogen salts $N_2F^+SbF_6^-$ and $N_2F_3^+Sb_2F_{11}^-$, and the dioxygenyl salt $O_2^+SbF_6^-$. The dioxygenyl salt is the most suitable oxidant for collecting ^{222}Rn in uranium mines, since it has negligible dissociation pressure at ambient temperature and releases oxygen as the gaseous reduction product. Reactions of this salt with radon and components of diesel exhausts (CO, CO_2, CH_4, SO_2, NO, and NO_2) have therefore been studied in some detail.[4,6] In this article, we report some properties of a new oxidant, $IF_6^+SbF_6^-$, which may also be suitable for applications in mines.

Seel and Detmer[7,8] have previously reported that two complexes are formed in the IF_7–SbF_5 system, one containing iodine and antimony in the ratio 1:3 and the other containing a higher proportion of iodine. The first complex was postulated to have the ionic structure $IF_4^{3+}(SbF_6^-)_3$; the second complex was postulated to be $IF_7 \cdot SbF_5$, although the solid actually isolated had far different composition, $IF_7 \cdot 2.4SbF_5$. Their findings have been questioned by Christe and Sawodny,[9] who point out that a structure involving IF_6^+ cation and polymeric $SbF_6^- \cdot xSbF_5$ anion is more probable than one involving IF_4^{3+} cation and SbF_6^- anion for the first product and that the observed stoichiometry may have been accidental for the second product.

We find that the 1:1 complex, $IF_6^+SbF_6^-$, can be obtained as a pure crystalline compound from mixtures containing excess IF_7. Spectral properties of the complex are similar to those of the analogous compounds $IF_6^+AsF_6^-$,[7-9] $ClF_6^+PtF_6^-$,[10-12] and $BrF_6^+AsF_6^-$.[13] We also find that a 1:2 complex, $IF_6^+Sb_2F_{11}^-$, exists in certain mixtures. Thus far, we have been unable to obtain this in a pure state.

Experimental Section

Materials and Equipment. Volatile compounds were handled in a Monel vacuum line fitted with a 0–1000 Torr bourdon gauge and Monel high-pressure valves (Autoclave Engineers 30VM-6071). High vacuum was provided by a Pyrex-glass line containing a three-stage oil diffusion pump. Stopcocks in contact with fluorine compounds were lubricated with Halocarbon 25-5S grease, and small vessels were sealed to the glass line with Halocarbon 8-00 wax, for dynamic pumping. Antimony pentafluoride (Allied Chemical Corp.) was vacuum distilled prior to use in a polychlorotrifluoroethylene still; iodine heptafluoride (B + A Division, Allied Chemical Corp.) was used as received. The purity of the compounds was checked by vapor pressure and infrared spectral measurements.

Preparation of $IF_6^+SbF_6^-$. In a typical preparation of the 1:1 complex, SbF_5 (58 mmol) was added to a tared nickel tube reactor (1.5 × 15 cm), which was sealed with a soft copper gasket and flare fitting attached to a Monel valve. Approximately one-half the theoretical amount of IF_7 was condensed into the reactor in vacuo at −195°, and the mixture was allowed to thaw. An exothermal reaction occurred below room temperature. The reactor was suspended in an oven, heated to 90–100° for 15 hr, and cooled again to room temperature. Very little IF_7 was found when the vessel was opened on the vacuum line. The inital product, a hard, caked solid, was removed with a chisel in a nitrogen-filled drybox, ground in a mortar, returned to the reactor, and heated again to 170–190° with excess IF_7 (48 mmol) for 15 hr. Unreacted IF_7 was then pumped off through a soda-lime trap at room temperature. The product, a dense, white, crystalline powder with a melting point of 175–180°, was removed and stored in the drybox. Anal. Calcd for $SbIF_{12}$: Sb, 25.54; I, 26.63; F, 47.83. Found: Sb, 25.58; I, 25.2; F, 47.0.

Elemental Analysis. Weighed samples of $IF_6^+SbF_6^-$ were hydrolyzed overnight in closed flasks with excess water. The solutions were made up to known volumes and analyzed as follows: **Sb.** One aliquot was treated with Na_2SO_3 to reduce antimony to the 3+ state. The solution was boiled to destroy excess SO_3^{2-} and was buffered with $NaHCO_3$. The antimony was then titrated with standard iodine solution. **I and F.** Antimony was removed from a second aliquot by precipitation as the sulfide. Excess S^{2-} was oxidized with basic H_2O_2. The solution was acidified and I^- was determined gravimetrically as PdI_2. Excess Pd^{2+} was then precipitated as $Pd(OH)_2$ and fluoride in the filtrate was titrated with thorium(IV) solution, using sodium alizarin sulfate indicator.

Examination of Other Solid Phases. Solid products obtained from 1:3 and 1:2 mixtures of IF_7 and SbF_5 were shown by X-ray powder patterns to consist of more than one phase. Raman spectra suggested that $IF_6^+Sb_2F_{11}^-$ was a principal product of the 1:2 mixtures.

Instruments. X-Ray powder patterns were obtained with a 114.6 mm diameter Philips camera and nickel-filtered Cu Kα radiation. Raman spectra were obtained with an instrument comprised of the following components: a Spex 1401 double monochromator; a Coherent Radiation Model 52 laser system providing helium–neon excitation at 6328 Å and argon excitation at 5145 Å; a Victoreen Model 1001 DC amplifier; and a Texas Instruments recorder. The optical system of this instrument has been described previously by Claassen et al.[14] Samples were examined in evacuated Pyrex tubes. Frequencies of the recorded bands were estimated to be accurate to ± 2 cm^{-1}.

Infrared spectra were obtained with a Beckman IR-12 spectrophotometer. Gases were contained in a 10 cm Monel cell with silver chloride windows, and solids were pressed between silver chloride plates or polyethylene plates protected by very thin films of Teflon. Silver chloride was attacked by $IF_6^+SbF_6^-$; the resulting window bands obscured some of the weak bands of the complex above 450 cm^{-1}.

Gaseous products formed in reactions of the complex with water, CO, CO_2, CH_4, SO_2, NO, NO_2, and Xe were analyzed with a Consolidated Engineering Corp. Model 21-620 mass spectrometer.

Density Measurements. The density of $IF_6^+SbF_6^-$ was measured by displacement of an inert fluorochemical (FC-75, 3M Co.) in a 1 cm^3 volumetric flask. It was found to be 3.48 g/cm^3 at 21°.

Volatility Measurement. A Pyrex vessel containing 620.2 mg of $IF_6^+SbF_6^-$ was attached to the high-vacuum line and dynamically pumped for 112 hr at ambient temperature (23–25°). During this period, the pressure dropped from 1×10^{-3} to 3×10^{-6} Torr. The loss in mass was 3.7 mg (0.60%).

Reaction with Liquid Water. $IF_6^+SbF_6^-$ hydrolyzed smoothly in excess water, producing a solution of HIO_4, $HSbF_6$, and HF. Gaseous IF_7, IOF_5, and HF were detected above the liquid phase in the initial stages of reaction, by mass spectral analysis; upon standing in closed vessels, these gases dissolved completely.

Reaction with KI Solution. Weighed samples of $IF_6^+SbF_6^-$ were hydrolyzed in 0.5 *N* HCl containing excess KI to determine the oxidizing capacity of the complex. Liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution. Eight equivalents of iodine would be expected for the reaction $IF_6^+SbF_6^- + 7I^- \rightarrow 4I_2 + 12F^- + Sb^{5+}$. An average value of 7.90 equiv/mol was found, based upon a molecular weight of 476.64. The oxidation state of antimony, which is highly pH dependent in the presence of iodide, was not determined but was assumed to have remained unchanged.

Reaction with Water Vapor. The effect of humid air on $IF_6^+SbF_6^-$ was determined as follows. Compressed air was passed through two bubblers in series containing water, then through glass U tubes containing 0.3 to 0.8 g of compound for 1.5 to 5.5 hr at ambient temperature. Off-gases were bubbled through either 0.1 *M* sodium hydroxide solution or acidified potassium iodide solution to recover volatile products. (These experiments simulated the decomposition of the compound in an air-filtering system. $IF_6^+SbF_6^-$ would normally be protected from moisture by a desiccant, but hydrolytic decomposition could occur if the desiccant were allowed to become depleted.) In two experiments with 0.6985 and 1.7608 mmol of the complex, 0.418 and 0.912 mmol of I^- and 3.605 and 6.790 mmol of F^-, respectively, were found in NaOH wash solutions (60 and 52% recovery of the total iodine). In three experiments with 0.6050, 0.7054, and 0.7081 mmol of $IF_6^+SbF_6^-$, 4.815, 4.938, and 5.477 mmol of iodine, respectively, were found in KI wash solutions, corresponding to 99.5, 87.5, and 96.7% of the amounts expected from the reduction of iodine(VII) compounds (IF_7 and IOF_5).

Reaction with Radon. Approximately 5 mCi of ^{222}Rn obtained from a radium chloride solution was condensed in a Pyrex flask at −195° with approximately 200 mg of $IF_6^+SbF_6^-$. The mixture was allowed to stand for 1 hr at room temperature. Radon was then shown to be fixed in the flask as a nonvolatile compound by measuring the γ emission of daughters ^{214}Pb and ^{214}Bi with a β–γ survey meter while pumping on the system with a diffusion pump. This technique for determining the volatility, and thus the chemical state of radon (i.e., element or compound), has been described previously.[3,15] The reaction of radon with $IF_6^+SbF_6^-$ was shown to occur very rapidly at 25° by further tests with packed beds of the complex and radon–air mixtures containing 122 to 210,000 pCi/l. of ^{222}Rn (simulated uranium mine atmospheres). A detailed description of these tests will be published elsewhere.

Behavior with a Xenon–Helium Mixture. A mixture of xenon and helium containing 57.0 mol % xenon was added to approximately 0.5 g of $IF_6^+SbF_6^-$ in an evacuated Pyrex flask to produce a total pressure of 200 Torr. The gas and solid were shaken intermittently for 3 hr at room temperature, and the gas was then analyzed mass spectrometrically. No change in composition was found. A similar result was obtained in a second experiment, when the bulb was heated to 60–62° for 1 hr. The oxidation potential of IF_6^+ is thus high enough to oxidize radon but not high enough to oxidize xenon.

Reactions with CO, CO_2, CH_4, and SO_2. Samples of carbon monoxide, carbon dioxide, methane, and sulfur dioxide (0.67 to 1.78 mmol), either undiluted or diluted with approximately equal volumes of helium, were passed through a glass U tube containing $IF_6^+SbF_6^-$ powder (approximately 3 mmol in each experiment). Product gases were collected in evacuated bulbs and analyzed mass spectrometrically. Carbon monoxide reacted smoothly with the powder, forming COF_2

Table I. X-Ray Powder Pattern of $IF_6^+SbF_6^-$

d, Å	*I*	$1/d^2$ obsd	$1/d^2$ calcd	*hkl*
4.226	10	0.0560	0.0543	110
3.553	1	0.0792		*a*
3.000	5	0.1111	0.1086	200
2.457	6	0.1657	0.1629	211
2.130	4	0.2204	0.2173	220
2.011	1	0.2473	0.2443	300, 221
1.909	8	0.2744	0.2715	310
1.744	2	0.3290	0.3258	222
1.615	9	0.3835	0.3801	321
1.509	1	0.4391	0.4344	400
1.425	5	0.4923	0.4887	411, 330
1.352	4	0.5472	0.5431	420
1.289	3	0.6023	0.5973	332
1.235	2	0.6555	0.6516	422
1.187	6	0.7103	0.7059	510, 431
1.105	3	0.8193	0.8146	521
1.070	1	0.8736	0.8687	440
1.039	2	0.9263	0.9231	530, 433
1.009	1	0.9824	0.9774	600, 442
0.983	2	1.035	1.032	611, 532
0.958	1	1.090	1.085	620
0.935	1	1.144	1.141	541
0.914	1	1.197	1.194	622
0.894	1	1.251	1.248	631
0.858	3	1.358	1.358	710, 550, 543
0.841	1	1.414	1.411	640
0.826	2	1.466	1.466	721, 633, 552
0.811	1	1.520	1.520	642
0.797	1	1.574	1.574	730

[a] Impurity.

and I_2; CO_2 and SiF_4 were also formed through reaction of COF_2 with the glass. In a typical experiment, a mixture consisting of (percent) CO (55.4), He (44.3), CO_2 (0.3), and O_2 (0.03) produced a gas consisting of CO (45.8), He (45.5), CO_2 (8.0), O_2 (0.04), COF_2 (0.4), and SiF_4 (0.3). Traces of iodine were also observed at mass 127, but most of the iodine was retained as a rust colored deposit in the $IF_6^+SbF_6^-$ powder. No reaction of CO_2 with $IF_6^+SbF_6^-$ was observed. Methane reacted to a negligible extent, producing trace amounts (0.1% or less) of CH_2F_2. Approximately 0.5 to 2% of the SO_2 was converted to SO_2F_2.

Reactions with NO and NO_2. Nitric oxide and nitrogen dioxide formed solid $NO^+SbF_6^-$ and $NO_2^+SbF_6^-$, respectively, in reactions with $IF_6^+SbF_6^-$.

In a typical experiment, 7.3 mmol of NO was added in three portions to an evacuated flask containing 1.9 mmol of $IF_6^+SbF_6^-$. The pressure dropped slowly after each addition. Forty minutes after the first addition, the residual gas was shown by mass spectral analysis to have the composition: NO, 0.6; SiF_4, 98; I_2, 0.2; and other components (N_2, CO, O_2, CO_2, N_2O, and NO_2), 1.2; 40 min after the last addition, it was shown to have the composition: NO, 82; SiF_4, 15; I_2, 0.5; and other components, 2.5. The vessel was evacuated with a mechanical pump for 66 hr at room temperature. The residual solid was then identified as $NO^+SbF_6^-$ by its Raman spectrum.[16]

In a typical experiment with NO_2, 4 mmol of the dioxide was condensed into a flask containing 0.572 g (1.20 mmol) of $IF_6^+SbF_6^-$ at −195°. The mixture reacted as it warmed to room temperature, producing a "wet" solid above 0°. Excess NO_2 and volatile products were pumped off with the mechanical pump over a period of 3 hr; 0.351 g (1.24 mmol) of solid product was obtained and was identified as $NO_2^+SbF_6^-$ by its Raman spectrum.[16] Samples of gas collected at several stages of reaction were found to have the following range of composition: NO_2, 25–88; SiF_4, 8–72; I_2, 0.5–1.0; and other components, 3.1–11.

Results and Discussion

Crystalline $IF_6^+SbF_6^-$ can be prepared from iodine heptafluoride and antimony pentafluoride as follows:

$$IF_7 + 2SbF_5 \xrightarrow[90-100°]{} IF_6^+Sb_2F_{11}^- \quad (1)$$

$$IF_7 + IF_6^+Sb_2F_{11}^- \xrightarrow[170-190°]{} 2IF_6^+SbF_6^- \quad (2)$$

The product of reaction 1 contains more than one solid phase but exhibits Raman bands at 340, 705, and 729 cm⁻¹, which are characteristic of the IF_6^+ cation,[9] and bands at 229, 295, 652, and 680 cm⁻¹, which are characteristic of the $Sb_2F_{11}^-$ anion.[13,16–18] Thus it consists chiefly of the 1:2 complex, $IF_6^+Sb_2F_{11}^-$. This same complex has been reported previously as a product of the oxidation of IF_5 by $KrF^+Sb_2F_{11}^-$.[19]

Table II. Vibrational Frequencies of $IF_6^+SbF_6^-$ and Their Assignments

Obsd freq, cm⁻¹ (intensity)		Assignment (point group)	
Raman	Infrared	IF_6^+ (O_h)	SbF_6^- (O_h)
	250 (m)	ν_6 (F_{2u})	
278 (10)			ν_5 (F_{2g})
	292 (m)		ν_4 (F_{1u})
339 (36)		ν_5 (F_{2g})	
	344 (m)	ν_4 (F_{1u})	
576 (6)			ν_2 (E_g)
	650 br (s)		ν_3 (F_{1u})
661 (47)			ν_1 (A_{1g})
682 (4)			
710 (100)		ν_1 (A_{1g})	
733 (24)		ν_2 (E_g)	
	797 (s)	ν_3 (F_{1u})	

Crystal Structure of $IF_6^+SbF_6^-$. The X-ray powder pattern of $IF_6^+SbF_6^-$ is shown in Table I. This has been indexed for a cubic unit cell with $a_0 = 6.069$ Å, $Z = 1$, and $V = 223.5$ Å³. The calculated density, 3.54 g/cm³, agrees fairly well with the experimental density, 3.48 g/cm³.

Zachariasen[20] has shown that in actinide fluorides with close-packed structure, each fluorine atom occupies a volume of 18 to 19 Å³. $IF_6^+SbF_6^-$ also conforms to this rule, with a volume per fluorine atom of 18.6 Å³.

Vibrational Assignments. The Raman and infrared spectra of the 1:1 complex strongly support the proposed ionic structure, $IF_6^+SbF_6^-$. Most of the observed bands (Table II) can be readily assigned to a compound containing two XY_6 ions of octahedral symmetry. The six normal vibrational modes of each ion are classified as $A_{1g} + E_g + 2\,F_{1u} + F_{2g} + F_{2u}$. The A_{1g}, E_g, and F_{2g} modes are Raman active, and the two F_{1u} modes are infrared active. The F_{2u} mode is both infrared and Raman inactive. All of the active modes have been observed for each ion, IF_6^+ and SbF_6^-, and have been assigned in a manner consistent with previous assignments for these ions.[9,16–18,21–24]

Chemical Properties. In contrast to most halogen fluoride–metal fluoride complexes, which react violently with water, $IF_6^+SbF_6^-$ hydrolyzes smoothly and exothermically.

$$IF_6^+SbF_6^- + 4H_2O \rightarrow HIO_4 + HSbF_6 + 6HF \quad (3)$$

This reaction occurs in several stages when the compound is exposed to humid air.

$$2IF_6^+SbF_6^- + H_2O \rightarrow IF_7 + IOF_5 + 2HSbF_6 \quad (4)$$

$$IF_7 + H_2O \rightarrow IOF_5 + 2HF \quad (5)$$

$$IOF_5 + 3H_2O \rightarrow HIO_4 + 5HF \quad (6)$$

Radon is rapidly oxidized by $IF_6^+SbF_6^-$ to a nonvolatile product, which remains fixed in the reagent bed. This has not been analyzed, since it has been prepared with only trace amounts of ^{222}Rn. By analogy with xenon, which forms $XeF^+SbF_6^-$ in the reaction with $N_2F^+SbF_6^-$, radon is believed to react as follows:

$$Rn + IF_6^+SbF_6^- \rightarrow RnF^+SbF_6^- + IF_5 \quad (7)$$

Carbon monoxide reacts with $IF_6^+SbF_6^-$ to form carbonyl fluoride. This reacts with glass to an appreciable extent, producing carbon dioxide and silicon tetrafluoride.

$$7CO + 2IF_6^+SbF_6^- \rightarrow 7COF_2 + 2SbF_5 + I_2 \quad (8)$$

$$2COF_2 + SiO_2 \rightarrow 2CO_2 + SiF_4 \quad (9)$$

No reaction has been observed between carbon dioxide and

$IF_6^+SbF_6^-$ at 23–25°. Methane and sulfur dioxide react to a slight extent with the complex, producing difluoromethane and sulfuryl fluoride, respectively.

$$CH_4 + IF_6^+SbF_6^- \rightarrow CH_2F_2 + 2HSbF_6 + 2IF_5 \quad (10)$$

$$SO_2 + IF_6^+SbF_6^- \rightarrow SO_2F_2 + IF_4^+SbF_6^- \quad (11)$$

Nitric oxide and nitrogen dioxide form the stable nonvolatile complexes $NO^+SbF_6^-$ and $NO_2^+SbF_6^-$, respectively, and the weak complexes $NO^+IF_6^-$ and $NO_2^+IF_6^-$. The latter decompose under dynamic vacuum.

$$2NO + IF_6^+SbF_6^- \rightarrow NO^+SbF_6^- + NO^+IF_6^- \quad (12)$$

$$NO^+IF_6^- \rightarrow FNO + IF_5 \quad (13)$$

$$2NO_2 + IF_6^+SbF_6^- \rightarrow NO_2^+SbF_6^- + NO_2^+IF_6^- \quad (14)$$

$$NO_2^+IF_6^- \rightarrow FNO_2 + IF_5 \quad (15)$$

Applications. Since $IF_6^+SbF_6^-$ is easily prepared from iodine heptafluoride and antimony pentafluoride, and since it has favorable properties, such as high oxidizing power, low dissociation pressure at ambient temperature, low corrosiveness to glass and fluorinated plastics, and high relative safety, we believe that it will prove useful for applications with radon. These may include (1) analysis of radon in air, (2) purification of contaminated air, and (3) separation of radon from lighter noble gases. Recent tests have shown that ^{222}Rn can be quantitatively collected from 5 to 10 l. of air with very small beds (3 to 10 g) of $O_2^+SbF_6^-$ or $IF_6^+SbF_6^-$. After radioactive equilibrium has been established, it is possible to measure the radon by counting γ-rays of daughters ^{214}Pb and ^{214}Bi. This method of analysis is currently being studied at Argonne. Although $O_2^+SbF_6^-$ and $IF_6^+SbF_6^-$ are decomposed by moisture, they can be used in conjunction with desiccants (calcium sulfate, silica gel, or molecular sieves) in humid atmospheres. Hence they can be used in filter devices ("breather vents") for trapping radon in mines. The high cost of drying humid air, either by chemical or refrigeration methods, is the principal limitation on their use in large continuous-circulation systems. Mixtures of noble gases can be separated by selective oxidation. For example, a mixture of krypton, xenon, and radon can be passed through a bed of $IF_6^+SbF_6^-$ to remove the radon, then through a bed of $O_2^+SbF_6^-$ to remove the xenon; the krypton will pass through unchanged. The radon and xenon can then be recovered by hydrolyzing the beds.

Acknowledgment. We thank I. M. Fox for chemical analyses and A. Engelkemeir for mass spectral analyses. F.A.H. thanks Argonne National Laboratory for a postdoctoral appointment.

Registry No. $IF_6^+SbF_6^-$, 55822-77-0; KI, 7681-11-0; ^{222}Rn, 14859-67-7; CO, 630-08-0; NO, 10102-43-9; NO_2, 10102-44-0; SbF_5, 7783-70-2; IF_7, 16921-96-3.

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Aminodifluoroborane

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Received September 24, 1974 AIC40696J

Aminodifluoroborane is the primary volatile product in the pyrolysis of ammonia–trifluoroborane at 185°. The new compound has an ionization potential of 12.4 ± 0.4 eV, and appearance potentials of principle ions from both aminodifluoroborane and aminoborane permit the calculation of $D(H_2N{-}BF_2) = 7.6$ eV, $D(H_2N{-}BH_2) = 8.1$ eV, $\Delta H_f(H_2NBF_2) = -255$ kcal/mol, and $\Delta H_f(H_2NBH_2) = -75$ kcal/mol.

Compounds containing B–N bonds are attractive monomers for the synthesis of thermally stable inorganic polymers. As an extension of previous work carried out in this laboratory on the isolation and characterization of aminoborane,[1] H_2NBH_2, and aminodichloroborane,[2] H_2NBCl_2, we have observed aminodifluoroborane produced from the pyrolysis of ammonia–trifluoroborane, H_3NBF_3.

Earlier studies of the pyrolysis of the ammonia–trifluoroborane adduct[3] reported the compound to be appreciably decomposed at 125° and the decomposition to be rapid at 150° according to $4NH_3{\cdot}BF_3 \rightarrow 3NH_4^+BF_4^- + BN$. There was no mention of intermediates. More recent work[4] contends that the decomposition is much slower, requires higher temperatures, and produces several H–N–B–F containing species, $NH_3{\cdot}BF_3 \rightarrow NH_4^+BF_4^- + [HNBF]_x$, but no boron nitride was reported. These reactions were complete in 36 hr at 252°.

In a similar case,[5] when diethylamine–trifluoroborane was heated at 250° the product was diethylaminodifluoroborane, $2(C_2H_5)_2NH{\cdot}BF_3 \rightarrow (C_2H_5)_2NH_2^+BF_4^- + (C_2H_5)_2NBF_2$. In this case the reaction is limited to the "extraction" of a molecule of hydrogen fluoride by a second molecule of the adduct. This appears to be the favored mode of reaction of most trifluoroborane adducts since there is no change in the number of strong B–F bonds and the activation energy is thereby diminished.[6]

Experimental Section

Ammonia–trifluoroborane was made from trifluoroborane etherate and ammonia in diethyl ether solution.[7] Small amounts of ammonium tetrafluoroborate remained in the finished product, but it did not