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The Synthesis of the Perfluoroammonium Cation, NF_4^+

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When a mixture of nitrogen trifluoride, fluorine, and antimony pentafluoride is heated under pressure, the salt NF_4SbF_6 is formed. It was characterized by evidence obtained from thermal decomposition, hydrolysis, elemental analyses, and fluorine nmr spectra. The salt is stable in a very dry atmosphere and at 200° *in vacuo* but decomposes rapidly above 300° to NF_3, F_2, and SbF_5. Hydrolysis of NF_4^+ quantitatively produces NF_3 and O_2 in a 2:1 mole ratio. The product as isolated from the Monel reactor is from 96 to 99% pure, the impurity being mainly $Ni(SbF_6)_2$. Fluorine nmr spectra obtained from *the salt dissolved in anhydrous HF were consistent with the presence of* SbF_6^- *and of a species of the type* $NF_x^{\pm,0}$. From this evidence the structure of the salt is $NF_4^+SbF_6^-$. Because the nmr spectra showed that all fluorines attached to nitrogen are equivalent, the NF_4^+ ion is almost certainly tetrahedral. The salt NF_4AsF_6 was also synthesized in a similar reaction and was characterized by the same methods of analysis. These results were quite analogous to those of the antimonate salt except that the thermal decomposition temperature was slightly lower and the purity was about 95%.

Introduction

In a recent communication,[1] the synthesis of the new cation NF_4^+ was described as resulting from the reaction of nitrogen trifluoride, fluorine, and antimony pentafluoride in liquid HF, at 200° and up to 85 atm in a Monel metal vessel. The product consisted of a mixture of NF_4SbF_6 and the antimonate and fluoride salts of metals from the reaction vessel.

This synthesis resulted from a systematic study of the NF_3–F_2–SbF_5–HF system in which it was thought that one or more of the possible NF_x^+ cations might be formed from NF_3. We have studied extensively a number of combinations of the components of the above quaternary system and have found, in addition to the reaction reported earlier, a second reaction in which the NF_4^+ cation is formed. These two reactions differ in that, in the first, a liquid phase of HF was present while, in the second, no HF was added to the system. The new reaction is

$$NF_3 + F_2 + SbF_5 \longrightarrow NF_4SbF_6 \qquad (1)$$

The reaction

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4AsF_6 \qquad (2)$$

also occurs under the same conditions. It has also been reported[2,3] that NF_3, F_2, and AsF_5 form NF_4AsF_6 when the reactants at low pressure are exposed to glow discharge.

Price, *et al.*,[4] on considering the NF_4^+ cation theoretically, concluded from its calculated electron affinity and size that it could not form crystalline salts. Wilson[5] estimated the heat of formation of NF_4^+ by comparing the isoelectronic series CF_2–CF_3–CF_4 and NF_2^+–NF_3^+–NF_4^+. From this and other considerations, he concluded that it was not unlikely that NF_4^+ could be prepared by a suitable ion-molecule reaction and observed in the gas phase. He also discussed the stability of hypothetical perfluoroammonium fluoride, perchlorate, sulfate, and fluoroborate. Of these, only the latter was thought possibly capable of existence and this only at low temperatures. He did not discuss the antimonate or arsenate salts in his paper but privately stated that these might very well be stable.

Prior to our experimental studies of the NF_3–F_2–SbF_5–HF system, we concluded that, if the series BF_4^-, CF_4, NF_4^+, and their trifluoride precursors had consistent properties, NF_4^+ might be considerably more stable than predicted. We also estimated[6] the heat of reaction to form the hypothetical salt $NF_4^+F^-$ in liquid HF. These conclusions and calulations encouraged us to attempt the preparation of NF_4SbF_6.

Nearly pure NF_4SbF_6 can be obtained under certain conditions. Variation of temperature and heating periods has produced salts having the compositions $NF_4Sb_2F_{11}$ and $NF_4Sb_3F_{16}$. It is likely that the complex anions $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ exist in these salts, since the fluorine nmr spectrum of $Sb_2F_{11}^-$ has been observed in other systems.[7-9] NF_4SbF_6 can be obtained from these salts, however, by heating them *in vacuo*.

The following describes the preparation, characterization, and some reactions of NF_4SbF_6 and NF_4AsF_6.

Experimental Section

Apparatus.—The vacuum system used in this work consisted of a metal manifold 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 nitrogen trifluoride.

All valves are Hoke M-482-M bellows valves. The fluorine line consists of copper lines and vessels fabricated with silver–copper eutectic solder. The multipurpose line is of Monel metal assembled by means of heliarc welding. Demountable joints were made from fittings having FEP Teflon ferrules.

The 60-cc reaction vessel is shown in detail in Figure 1. Ves-

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(1) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Nucl. Chem. Letters*, **2**, 79 (1966).

(2) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *ibid.*, **2**, 83 (1966).

(3) J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).

(4) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.*, **35**, 201 (1963).

(5) J. N. Wilson, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p 30.

(6) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, paper presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(7) W. E. Tolberg, R. S. Stringham, R. E. Rewick, and M. E. Hill, Technical Progress Report No. 7, Stanford Research Institute, April 30, 1965, Contract AF-04(611)-9370.

(8) R. J. Gillespie, private communication.

(9) J. K. Ruff, *Inorg. Chem.*, **5**, 1791 (1966).

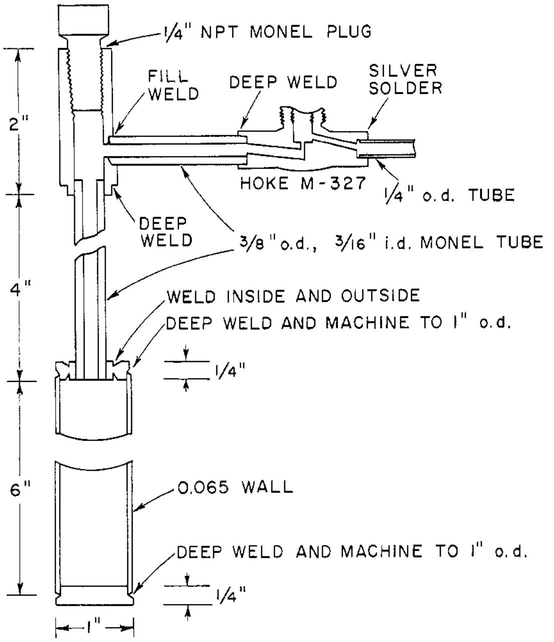

Figure 1.—Monel reaction vessel.

sels were fabricated by means of heliarc welding and were tested under vacuum with a helium leak detector, treated with fluorine gas, and later tested at 200 atm with nitrogen gas.

Reagents.—Nitrogen trifluoride was obtained 99.9% pure from Air Products Co. A 2.25-l. atm amount was condensed at liquid nitrogen temperature, warmed to −130°, transferred to the calibrated volume at −196°, and pumped on.

Fluorine with a typical analysis of 98% purity was obtained from Allied Chemical Corp. A 3-l. atm sample was condensed into a trap packed with nickel spirals and cooled to −196°. The gas remaining in the metering volume was isolated from the trap, and the contents of the trap volatile at −196° were transferred to a 1-l. volume cooled to −210°. On isolation from the trap, the liquid was pumped on at −210° (solid nitrogen–liquid nitrogen slush), warmed to −196°, and transferred into the calibrated volume at −210°.

Antimony pentafluoride was obtained 99.5% pure from Allied Chemical Corp. It was transferred directly from the supply vessel into an FEP Teflon buret by trap-to-trap distillation. The contents of the buret were pumped on at −44° and used without further purification.

Hydrogen fluoride was obtained in excellent purity from Olin Corp. Because HF reacts slowly with its container forming hydrogen gas, the hydrogen is removed to facilitate vacuum transfer. Before use the HF was treated with fluorine to eliminate impurities such as water that can react with NF_4^+ salts. The fluorine is removed by pumping on the HF cooled to −196°.

Experimental Techniques.—The volumes of all sections of the multipurpose line were measured by expansion of a known pressure of nitrogen from a known volume. The vacuum system was maintained leak-free by testing with a helium leak detector. The combination of reagents HF, F_2, and SbF_5, although highly corrosive, appears to passivate the system.

Fluorine behaves as a perfect gas in the pressure range up to 13 atm (gauge limit) and was measured in the calibrated volume at sufficient pressure to obtain about 0.13 mole.

Nitrogen trifluoride does not behave as a perfect gas over the same pressure range. Consequently, its deviation from perfect gas law behavior was determined and used to obtain measurement of the quantity of NF_3 supplied to the reaction vessel.

Antimony pentafluoride was measured only approximately by volume because in a metal system treated with fluorine much SbF_5 is lost by reaction with metal fluorides to form antimonate salts. The Monel reaction vessel also absorbed several grams of SbF_5 when exposed to fluorine at high pressure and 200°.

In a typical preparation of NF_4SbF_6, 0.07 mole of SbF_5 and 0.09 mole of NF_3 were condensed into the reaction vessel at −196° while 0.13 mole of F_2 was condensed from the calibrated volume at −196° into the reaction vessel at −210°. The reaction vessel was placed in a vertical tube furnace surrounded by Fiberglas and enclosed in a steel safety shield. The temperature was obtained from an iron-constantan thermocouple The reaction mixtures were heated at 100° or at 200° for from 24 to 124 hr.

In preparations involving the quantities of reactants given above at 200° and 50 hr, about 41% of the NF_3 initially present is consumed. The consumption of NF_3 drops to 11% at 100° for 50 hr. The amount of F_2 consumed always exceeds the amount of NF_3 consumed because of reaction of F_2 with the container.

The NF_4^+ salts react readily with moisture in the atmosphere but are stable indefinitely in the nitrogen atmosphere provided by a Vacuum Atmosphere Corp. drybox equipped with a recirculation system that removes both oxygen and water.

Preparation of NF_4AsF_6.—NF_3, F_2, and AsF_5 were heated at an initial pressure of 2000 psi for 260 hr at 125°. About 12% of the NF_3 was converted to a solid product that, when heated to 300°, decomposed to yield approximately equimolar quantities of the starting reagents. Hydrolysis of 0.5 g of the salt yielded NF_3 and O_2 in an approximately 2:1 mole ratio. No oxides of nitrogen were detectable by mass spectrometry. The sample was about 95% pure.

Analyses.—The procedure is here outlined for safely removing unreacted starting materials from the reactor on completion of the heating period and for subsequent analysis of the NF_4^+ salts formed in the reaction. After 50 hr of heating at 200°, the pressure of unreacted F_2 and NF_3 in the reaction vessel is in excess of 30 atm. Because fluorine even at pressures as low as 2 atm cannot always be released through a small valve into an evacuated system without the occurrence of a fluorine fire in the valve, the reactor is cooled to −196°, the valve is opened, and the reactor is warmed to −130°. The F_2 and NF_3 are transferred into a 500-cc vessel and warmed to room temperature, and the pressure is recorded.

The mixture is condensed again in the 500-cc volume at −210° and the fluorine is removed by pumping on the system. The fluorine is disposed of slowly through a scrub vacuum line which is equipped with a Sodasorb trap. Complete separation of fluorine requires repeated warming of the mixture to room temperature, measurement of pressure, cooling to −210°, and pumping. A constant pressure is usually observed after the third extraction. The gas remaining is NF_3 containing a small but detectable quantity of both CF_4 and SiF_4. Since neither is dedetectable by infrared spectra of the starting materials, it is assumed that they are derived from the reaction vessel. The impurities present, however, do not contribute appreciable error to the determination of F_2 and NF_3 from pressure readings obtained as described above.

The reactor is cut open with a hack saw within the drybox and the NF_4^+ antimonate and complex antimonate salts (>15 g) are safely removed from the reactor by breaking up the melt and scraping it out.

Reaction with SiO_2.—Because water and the elements of water are extremely difficult to remove from glass, it was necessary to observe the interaction of NF_4SbF_6 with glass to determine the feasibility of obtaining X-ray powder diffraction patterns in glass capillaries. As expected, the reaction of very dry glass with NF_4SbF_6 resembled hydrolysis until the elements of water were depleted. When the temperature was increased to 85°, a different reaction occurred, yielding NF_3 and SiF_4 but no oxygen. It was assumed that O_2SbF_6 was formed. At higher temperatures, the Monel vessel was attacked and metal oxides were formed. Thus it appears that X-ray spectra can be obtained only with special treatment of the glass capillaries to avoid partial decomposition of the sample.

Reaction with Halides.—Attempts to obtain infrared spectra from NF_4SbF_6 in pressed pellets of KBr and KCl produced spectra showing that NF_4^+ reacts readily with the bromide, but slowly with the chloride. In addition, the salt did not etch a polished silver chloride plate.

Nmr Spectra.—F^{19} resonance spectra were obtained from NF_4SbF_6 and NF_4AsF_6 dissolved in HF and contained in FEP Teflon capsules. The capsules fit inside standard nmr tubes and have an i.d. of 0.100 in. The spectrometer is a Varian Associates Model HA-100, operated in the HR mode at 94.1 Mcps.

Solubility in HF.—NF_4SbF_6 is quite soluble in HF, but the Monel salt impurities have a low solubility. Thus, the NF_4SbF_6 was easily purified by filtration. The solubility of NF_4SbF_6 purified in this manner was 2.6 g/g of HF. The solubility of similarly purified NF_4AsF_6 is 1.2 g/g of HF. Relative intensities of nmr lines show that solubility decreases with decreasing temperature.

Thermal Decomposition.—NF_4SbF_6 is thermally stable at 200° but decomposes rapidly above 300° according to the reaction

$$NF_4SbF_6 \longrightarrow NF_3\uparrow + F_2\uparrow + SbF_5$$

The decomposition was carried out in a Monel vessel heavily passivated with respect to F_2 and SbF_5. The F_2 and NF_3 were recovered quantitatively in a 1:1 mole ratio (approximately 49% NF_3 and 48% F_2), but only a small quantity of the SbF_5 was observed, the balance having been taken up by the metal vacuum lines.

Hydrolysis.—Weighed samples (0.5 g) of the product were hydrolyzed in 1–2 ml of water. The hydrolysis is a smooth reaction proceeding according to the equation

$$NF_4^+ + H_2O \longrightarrow NF_3\uparrow + {}^1/_2O_2\uparrow + H_2F^+$$

The NF_3 and O_2 were determined by the method described for NF_3 and F_2. The ratio of NF_3 to O_2 was 2:1 with a precision of 2 parts in 200. Mass spectrometric analysis of the gases evolved showed only NF_3 and O_2; no other gases such as nitrogen oxides were detectable. The hydrolysis of the anion(s) is complex and is complete in strong base.[10] The hydrolysate was later analyzed for antimony by bromate titration,[11] with the modification that borate was added to eliminate interference by fluoride ion. Fluoride was determined colorimetrically.[12] Because the product is contaminated with salts from the Monel metal container, the sample was also analyzed for Ni^{2+} and Cu^{2+}. The contamination by copper which might reasonably be expected to occur in a Monel vessel was usually negligible.

The elemental analysis performed as above indicates the presence of complex fluoroantimonate anions. When mixtures from various preparations were heated at 200° for 3 days, they analyzed quantitatively from 96.0 to 99.5% NF_4SbF_6 and the balance was $Ni(SbF_6)_2$. These purities represent a range observed in 12 preparations, and the quality of preparations improved as our work progressed. *Anal.* Calcd for NF_4SbF_6: N, 4.30; Sb, 58.33; F, 37.37. Found: N, 4.27 ± 0.04; Sb, 57.85 ± 0.06; F, 37.64 ± 1.5; Ni, <0.30.

Results and Discussion

The interaction of NF_3, F_2, and SbF_5 has been studied under varying conditions of temperature, pressure, and proportion of starting materials. The product is NF_4SbF_6 contaminated with a small percentage of metal antimonate salts from the reaction vessel. This conclusion is based on elemental analysis, identity and quantity of products from hydrolysis, thermal decomposition, and nmr spectra.

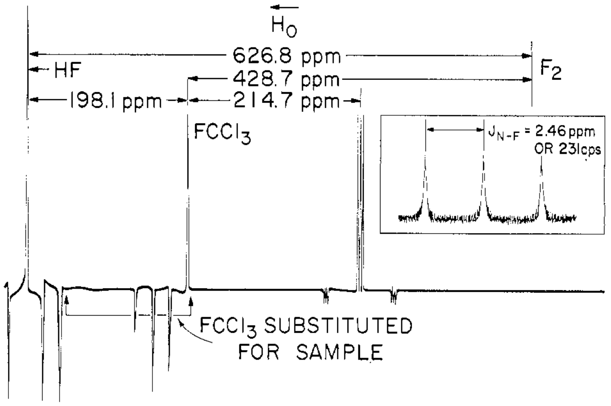

Figure 2.—Nmr spectrum of NF_4SbF_6.

The F^{19} nmr spectra of the reaction product dissolved in HF (Figure 2) consisted of a triplet at −214.7 ppm from $FCCl_3$ and a broad line obscured by the side bands downfield from HF. The latter appears to be characteristic of SbF_6^-, while the triplet differs from any known NF compound. The triplet was assigned to NF_4^+ as follows. (1) The resonance triplet having lines of equal intensity can arise from the interaction of F^{19} with a nucleus having unit quadrupole moment. (2) The triplet no longer appears after the product has been thermally decomposed and has evolved equivalent quantities of both NF_3 and F_2. Thus since nitrogen has a quadrupole moment of 1, the triplet is due to the presence of a structure of the type $NF_x^{\pm,0}$. Exclusion of paramagnetic structures and those having more than eight electrons in the bonding orbitals allows only NF, NF_2^-, and NF_4^+. (3) The hydrolysis of the product evolves NF_3 and O_2 while NF_3, N_2F_2, and the ionic complexes N_2FAsF_6[13] and $N_2F_3Sb_2F_{11}$ all produce oxides of nitrogen. (The hydrolysis of the gases is slow, while that of the ionic compounds is rapid, $N_2F_3Sb_2F_{11}$ hydrolyzing explosively at room temperature.) In addition, evolution of NF_3 and O_2 in a ratio of 2:1 on hydrolysis shows that the oxidation number of nitrogen in the allowed NF species is 5. NF_4^+ is the only one of the allowed structures that has the proper valence and that could produce NF_3 on hydrolysis. If NF_4^+ is present as shown above, the compound has the structure $NF_4^+SbF_6^-$.

The existence of the $NF-F^{19}$ triplet and no other resonance attributable to an NF structure shows that all fluorines in NF_4^+ are equivalent and that the structure of the ion is almost certainly tetrahedral as expected.

Fluorine nmr spectra were obtained on numerous reaction products as well as on products converted to NF_4SbF_6 by heating *in vacuo*. No resonance lines other than those attributable to NF_4^+ in the form of its antimonate or complex antimonate salts have been observed. The combined evidence from nmr spectra, hydrolysis, and analysis of unreacted starting materials shows that NF_3 undergoes no reactions other than those leading to formation of NF_4^+.

Some questions have been raised by Guertin, *et al.*,[3] concerning the preparation of NF_4^+ salts by the above described method. The assertion was made that the

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glow discharge yields NF_4AsF_6 in high purity while the high-temperature, high-pressure method does not. Because their reported hydrolysis of the glow-discharge product yielded "very large quantities of nitrogen oxides or nitrogen oxygen fluorides," we deduce that their product contained very large quantities of impurities. This is based on the fact that we found unequivocally no nitrogen oxides and only NF_3 and O_2 on hydrolysis of either NF_4AsF_6 or NF_4SbF_6 from our reactor. This evidence and the product analyses make it clear that the reaction under high pressure and elevated temperature yields a product of known high purity and in quantity.

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The Difluorochlorate(I) Anion, ClF_2^-. Vibrational Spectra and Force Constants

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The vibrational spectra of complexes containing the difluorochlorate(I) anion, ClF_2^-, confirm the linear, centrosymmetric structure of ClF_2^- (point group $D_{\infty h}$) in $NOClF_2$. However, infrared spectra indicate distortion and/or lowering of the site symmetry of ClF_2^- in $RbClF_2$ and $CsClF_2$, the result of crystal field effects. The valence force and coupling constant of ClF_2^-, calculated by using the linear, centrosymmetric structure, are 2.35 and 0.17 mdynes/A, respectively. The bonding in ClF_2^- is best explained by a semiempirical molecular orbital model involving mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center, four-electron pσ bond. Valence force constants are confirmed to be generally applicable for the characterization of semiionic 3c–4e (three-center, four-electron) bonds. However, it is suggested that these bonds do not necessarily require unusually high positive values for the coupling constants. There is a correlation between the single-bond order values and the valence force to coupling constant ratio for a series of electronically similar XY_2 groups. The unusually high positive values of the coupling constant of some of the members seem to be due to additional ionic contributions to the over-all potential energy in excess of the amount required for the formation of semiionic bonds.

Introduction

The existence and properties of the difluorochlorate(I) anion, ClF_2^-, have been reported recently.[2-4] Since only one stretching vibration had been observed for this anion in the infrared spectra of its nitrosonium[2] salt, it was suggested that ClF_2^- is linear rather than bent. However, no definite conclusion about the molecular structure could be reached without knowledge of the Raman spectrum. Furthermore, the data available were not sufficient to select the correct bond model.[2-4] Since the knowledge of the Raman spectrum also allows the calculation of force constants and thereby a choice between the different bond models, the recording of this spectrum appeared to be very desirable.

Experimental Section

The preparation of $KClF_2$ and $RbClF_2$ has been previously described.[3] The assays of $KClF_2$ and $RbClF_2$ were 27 and 49%, respectively, the remainder being the corresponding alkali metal fluoride.[3]

Raman spectra of the solids were recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 A) as exciting line and a saturated KNO_2 solution as a filter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thickness were used.

Infrared spectra of the solids, $RbClF_2$ and $CsClF_2$, were recorded on a Beckman IR-9 prism-grating spectrophotometer in the range 4000–400 cm^{-1}. Dry powder and Nujol or hexafluorobenzene mull techniques were used. Samples were placed between AgCl plates held in place by a screw-cap metal cell equipped with neoprene O rings.

Owing to their hygroscopic nature, the ClF_2^- salts were handled in the dry nitrogen atmosphere of a glove box.

Results and Discussion

Figure 1 illustrates the Raman spectrum of solid $KClF_2$. It is very similar to that of solid $RbClF_2$. Both spectra show only one line (very strong intensity) at 475 and 476 cm^{-1}, respectively. Whereas the quality of the infrared spectra of the alkali metal difluorochlorates(I) was somewhat poor, the Raman spectra were of good quality, even that of the $KClF_2$ sample, which contained only 27% difluorochlorate(I) salt,[3] the remainder being KF.

A triatomic ion such as XY_2^- could be either linear or bent, symmetric or asymmetric. Linear sym-

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[1] Visiting Scientist from the Institut für Anorganische Chemie, Technische Hochschule, Stuttgart, Germany.

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[4] K. O. Christe and J. P. Guertin, paper presented at the Third International Fluorine Symposium, Munich, Germany, Aug 1965.