agreement with those obtained from the variation of dissociation constant with dielectric constant in solvent mixtures.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., CANADA]

Some Salts of Trifluoromethylfluoroboric Acid[1,2]

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Trimethyltrifluoromethyltin reacts with boron trifluoride to give a 1:1 adduct, formulated as trimethyltin trifluoromethylfluoroborate, $(CH_3)_3Sn^+$, $[CF_3BF_3]^-$. The potassium, barium and ammonium salts of the hypothetical trifluoromethylfluoroboric acid HBF_3CF_3 are prepared from this adduct. The stability of the ion $[CF_3BF_3]^-$ is attributed to the saturation of the acceptor tendencies of the boron atom and the delocalization of the charge on the ion.

We have previously described the preparation of trimethyltrifluoromethyltin by the reaction of hexamethylditin with trifluoroiodomethane[3,4]

$$(CH_3)_3Sn-Sn(CH_3)_3 + CF_3I \longrightarrow (CH_3)_3SnCF_3 + (CH_3)_3SnI$$

Differences in behavior between this compound and analogous known perfluoroalkyl compounds of other elements were ascribed to the electropositive nature of the tin atom, leading to polarization of the $Sn-CF_3$ bond. It was therefore of interest to investigate the reaction of trimethyltrifluoromethyltin with strong electron acceptor molecules, in the hope of inducing complete heterolytic fission of the $Sn-CF_3$ bond and the production of complex salts containing the trimethyltin cation. Other workers[5] have reported that alkyl-perfluoroalkyl tin compounds release alkyl rather than perfluoroalkyl groups on treatment with electrophilic reagents (H^+ or BCl_3, etc.) and described this result as surprising.

We have now found that trimethyltrifluoromethyltin reacts readily with boron trifluoride to form a 1:1 adduct, whose properties clearly indicate that it should be formulated as trimethyltin trifluoromethylfluoroborate, $(CH_3)_3Sn^+ [CF_3BF_3]^-$.

When a mixture of trimethyltrifluoromethyltin and boron trifluoride was allowed to warm up from -196 to 20°, a reaction occurred rapidly with the production of solid material, but considerable darkening was also noticed and a pure product could not be isolated. It was found, however, that reaction in carbon tetrachloride solution immediately precipitated the insoluble white adduct; recovery of excess boron trifluoride showed that equimolar quantities had reacted. The complex was extremely hygroscopic and was handled in a dry atmosphere. On keeping it slowly decomposed, darkening in color and evolving boron trifluoride.

The analogous phosphorus compound $(CH_3)_2PCF_3$ also forms with boron trifluoride a 1:1 adduct, which has been formulated as a simple molecular addition compound involving donation from the phosphorus to the boron atom.[6] Such coördination must be considered very unlikely for trimethyltrifluoromethyltin, however, since no electrons are available on the tin atom for donation.

The formation of an adduct with an ionic structure would occur by removal of the trifluoromethyl group from the tin atom as CF_3^-, giving the familiar trimethyltin cation and the trifluoromethylfluoroborate anion $[CF_3BF_3]^-$. This is the first example to be reported of such transfer of a trifluoromethyl group and demonstrates clearly the pseudo-halogen character of this group. Complex anions derived from the perfluoroalkyl mercurials are known,[7] such as $[(CF_3)_2HgI_2]^-$, but these are formed by transfer of a halide ion rather than a trifluoromethyl group. The heterolytic fission of the $Sn-CF_3$ bond will be facilitated by the electropositive nature of the tin atom and in particular by the stability of the trimethyltin cation. It seems probable, therefore, that similar reactions may occur between acceptor molecules and perfluoroalkyl derivatives of other electropositive elements, such as lithium, magnesium and zinc; this is being investigated.

The trifluoromethylfluoroborate anion has not been reported previously; indeed no stable compound containing a trifluoromethyl-boron linkage is known despite much work in this field. Because of the strong acceptor properties of boron, it has been suggested[8] that simple perfluoroalkyl derivatives of trivalent boron would be unstable, and this is supported by the reported decomposition of the compound $CF_2{:}CFBCl_2$ to give boron trifluoride.[5] In the trifluoromethylfluoroborate ion, however, the acceptor properties of the boron atom are fully satisfied, conferring stability on the ion.

Trimethyltin trifluoromethylfluoroborate is freely soluble in water, giving a stable solution, and this property was used to prepare other salts of the hypothetical trifluoromethylfluoroboric acid HBF_3CF_3. The potassium salt, which was used for most of the studies made, was prepared by adding potassium fluoride to a solution of the trimethyltin salt, when insoluble trimethyltin fluoride was precipitated and evaporation of the resulting solution gave potassium trifluoromethylfluoroborate.

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[1] This work was supported by the U. S. Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

[2] For a preliminary communication see R. D. Chambers, H. C. Clark and C. J. Willis, *Proc. Chem. Soc.*, 114 (1960).

[3] H. C. Clark and C. J. Willis, THIS JOURNAL, **82**, 1888 (1960).

[4] R. D. Chambers, H. C. Clark and C. J. Willis, *Chem. and Ind. (London)*, 76 (1960).

[5] H. D. Kaesz, S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **81**, 6336 (1959).

[6] M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **38**, 119 (1960).

[7] H. J. Emeleus and J. J. Lagowski, *J. Chem. Soc.*, 1497 (1959).

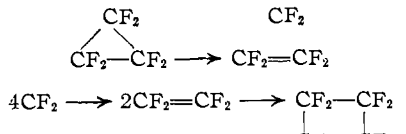
[8] J. J. Lagowski and P. G. Thompson, *Proc. Chem. Soc.*, 301 (1959).

$$(CH_3)_3Sn(CF_3BF_3) + KF \longrightarrow K(CF_3BF_3) + (CH_3)_3SnF$$

It was found that dilute solutions of the free acid were stable, enabling the barium and ammonium salts to be prepared by using an ion-exchange resin column.

The potassium salt was freely soluble in water, in contrast to potassium fluoroborate and the potassium salts of other strong acids. It was not, however, hygroscopic, as were all the other salts made. It showed a high degree of thermal stability and did not decompose when heated *in vacuo* to 300°. Above this temperature decomposition began and tetrafluoroethylene was produced, together with small amounts of perfluorocyclopropane and perfluorocyclobutane. The solid residue was identified as potassium fluoroborate.

These products clearly arise through the transfer of fluorine from carbon to boron in the trifluoromethylfluoroborate ion, accompanied by the elimination of difluoromethylene. Under the low pressure used in this pyrolysis tetrafluoroethylene was the major volatile product. In the thermal decomposition of trimethyltrifluoromethyltin at 150° high yields of perfluorocyclopropane were obtained, but in that case the pyrolysis was carried out in a sealed tube at 4–5 atmospheres pressure, conditions which would clearly favor the further reaction of tetrafluoroethylene with difluoromethylene. When potassium trifluoromethylfluoroborate was pyrolyzed in a sealed tube at 450° the volatile product was mainly perfluorocyclobutane with some perfluoropropylene and other olefins. Perfluorocyclopropane was not found, but a separate experiment showed that it is not stable at this temperature, decomposing to perfluorocyclobutane, perfluoropropylene and other fluoroölefins. Perfluorocyclobutane, the major product of this decomposition, presumably arises through the decomposition of the three-membered ring to tetrafluoroethylene and difluoromethylene.



Ammonium trifluoromethylfluoroborate was found to be less stable than the potassium salt. On heating *in vacuo* some volatile material was evolved above 150° and at 175° rapid decomposition occurred, giving tetrafluoroethylene and ammonium fluoroborate as major products.

Solutions of the hypothetical trifluoromethylfluoroboric acid HBF_3CF_3 were prepared by passing any of its salts through a cation exchange column. Such solutions were stable to prolonged boiling, showing no increase in acidic content. Alkaline solutions of the trifluoromethylfluoroborates were also stable to boiling, but the ion was destroyed by boiling with 50% sulfuric acid, when 5.5–5.7 of the six fluorine atoms in the molecule appeared as fluoride ion. Fluoroform was not found.

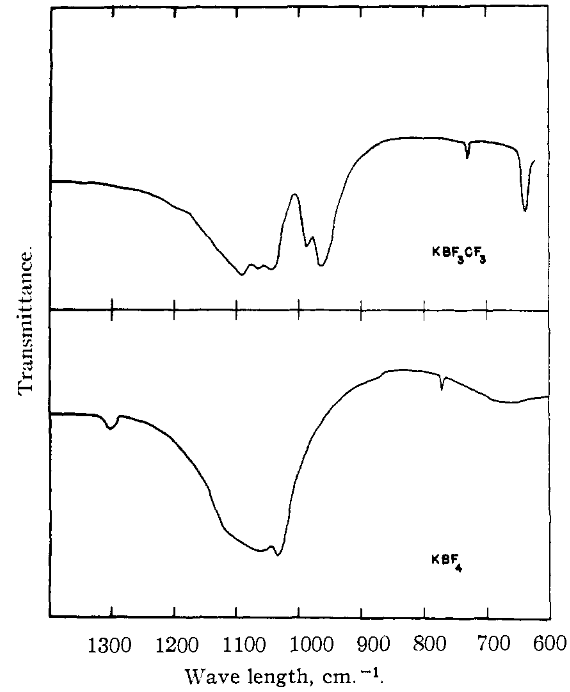


Fig. 1.

The destruction of the stable trifluoromethyl group on hydrolysis, giving fluoride ion, is unusual, because this group is usually the most electronegative center in the molecule and therefore is eliminated as fluoroform. In the trifluoromethylfluoroborate anion it might have been thought possible that the negative charge, which formally rests on the boron atom, could be transferred to the carbon atom or to one of the fluorine atoms attached to the boron, *e.g.*

$$CF_3\overset{-}{B}F_3 \longleftrightarrow \overset{-}{C}F_3\ BF_3 \longleftrightarrow CF_3BF_2\ \overset{-}{F}$$

The removal of a trifluoromethyl group in this manner would be the reverse of the process by which the ion was formed. The hydrolysis studies, however, indicate that such an equilibrium is unlikely to obtain, since if there were any tendency for the trifluoromethyl group to be removed as CF_3^- it would render the ion liable to attack in acid solution with consequent production of fluoroform.

$$\overset{-}{C}F_3BF_3 + H_3\overset{+}{O} \longrightarrow CF_3H + H_2O\cdot BF_3$$

It appears more likely that the negative charge on the boron is transferred through the carbon atom to the fluorine atoms of the trifluoromethyl group.

The infrared spectra of the trifluoromethylfluoroborates were of considerable interest. The potassium, barium and ammonium salts showed very similar absorption bands in the region 600–1200 cm.$^{-1}$, showing that as with ammonium fluoroborate[9] no hydrogen-bonding was present in the ammonium salt. The spectrum of the potassium salt is shown in the figure, together with that of potassium fluoroborate. Absorption bands were present at 637, 737, 963, 985, 1041, 1063 and 1090 cm.$^{-1}$; the weak bands previously reported at 882 and 687 cm.$^{-1}$ were not present in carefully purified samples. The spectrum of potassium fluoroborate has been closely studied by Cote and Thompson,[9] who assign the strong absorptions in the region 1040–1090 cm.$^{-1}$ to asymmetric B–F stretching frequencies, and the

(9) G. L. Cote and H. W. Thompson, *Proc. Roy. Soc.* (*London*), **210**, 217 (1951).

very similar absorption in potassium trifluoromethylfluoroborate may therefore be similarly assigned. Absorptions associated with C–F stretching frequencies are usually found between 1100 and 1350 cm.$^{-1}$, but in the trifluoromethylfluoroborates no bands are noticed in this region. We suggest, therefore, that the strong absorptions at 962 and 985 cm.$^{-1}$ are associated with the C–F stretching vibrations, the shift to lower frequencies being due to the negative charge on the ion and the consequent decrease of the force-constants of the carbon–fluorine bonds. A comparable shift is found between boron trifluoride and the fluoroborate ion. In the former, strong absorption bands associated with the asymmetric B–F stretching vibrations are found at 1446 and 1497 cm.$^{-1}$,[10] whereas in the latter they are displaced to the region 1050–1100 cm.$^{-1}$.

The fluorine nuclear magnetic resonance spectrum of the trifluoromethylfluoroborate ion has also been studied and found to be fully consistent with the proposed structure. It will be reported elsewhere fully.

The high degree of stability which has been found for the trifluoromethylfluoroborate ion may be ascribed to two factors: (1) the filling of the vacant orbitals on the boron atom with its expansion to tetracoördination (2) the shielding effect resulting from the distribution of the negative charge over all six fluorine atoms in the ion. In simple perfluoroalkyl boron derivatives, such as trifluoromethylboron difluoride, CF_3BF_2, neither of these effects could occur. Until such compounds are prepared, however, it will remain an open question whether the absence of such stabilizing influences will contribute to a reduction from the high stability of the anion to a level where spontaneous decomposition will occur.

Experimental

As in previous work,[3] standard techniques for the manipulation of volatile compounds were used. Infrared spectra were recorded on a Perkin–Elmer model 21 spectrophotometer with sodium chloride optics.

Trimethyltrifluoromethyltin.—Hexamethylditin (15.8 g., 48 mmoles, prepared as described previously[3]) was introduced into a Pyrex Carius tube (100 ml.) and after freezing and evacuating the tube trifluoroiodomethane (57.8 g. 296 mmoles) was condensed on. The tube was allowed to warm to 20° and then irradiated for 6 hr. at a distance of 6″ from a 250 watt ultraviolet lamp. The tube was shielded to permit irradiation of the liquid phase only. Fractionation of the contents then gave unchanged trifluoroiodomethane, trimethyltrifluoromethyltin (7.8 g., 70% yield, b.p. 101°) and impure trimethyltin iodide (12.2 g.). In larger scale preparations handling losses were reduced and yields of trimethyltrifluoromethyltin of over 80% were obtained.

Reaction with Boron Trifluoride.—Trimethyltrifluoromethyltin (2.01 g., 8.6 mmoles) was dissolved in anhydrous carbon tetrachloride (13 g.) and boron trifluoride (0.717 g., 10.5 mmoles) was condensed on. On warming the tube, immediate reaction occurred as the carbon tetrachloride melted, with precipitation of a white solid. After 1 hr. at 20° the tube was opened and volatile materials were found to be unreacted boron trifluoride (0.155 g., 2.3 mmoles) and fluoroform (0.024 g., 0.3 mmole). The adduct was filtered off in a dry atmosphere and washed with carbon tetrachloride. On heating the adduct with 10% aqueous sodium hydroxide for 15 hr. at 100° trace quantities of fluoroform were detected spectroscopically. Samples of the adduct were distilled with 50% sulfuric acid ("fluosilicic acid" distillation) and fluoride in the distillate estimated as lead chlorofluoride in the usual way, when fluorine corresponding to 5.7 of the six fluorine atoms in the molecule was found.

Anal. Calcd. for $C_4H_9SnBF_6$: F, 37.9. Found: F, 36.1.

Potassium Trifluoromethylfluoroborate.—Trimethyltin trifluoromethylfluoroborate (2.20 g., 7.3 mmoles) dissolved in water (20 ml.) and potassium fluoride (0.425 g. 7.3 mmoles) in water (20 ml.) was added. The solution was boiled for 30 min. and the precipitate of trimethyltin fluoride removed by filtration and identified spectroscopically. The filtrate was evaporated to dryness. The residue was dissolved in a small amount of water and filtered, the filtrate evaporated to dryness and the potassium salt recrystallized from ethanol.

When the potassium salt was distilled with 50% sulfuric acid, fluoride ion corresponding to 5.5 of the six fluorine atoms was found in the distillate. This figure was unchanged on further recrystallization.

Anal. Calcd. for KBF_3CF_3: K, 22.2; F, 64.8. Found: K, 22.9; F, 59.2.

In later preparations it was found convenient to prepare the aqueous solution of trimethyltin trifluoromethylfluoroborate by extracting with water the suspension of the salt in carbon tetrachloride.

Barium Trifluoromethylfluoroborate.—A solution of trifluoromethylfluoroboric acid was prepared by passing a solution of the trimethyltin salt through the acid form of a cation exchange resin column (Dowex 50-W). The acid was then neutralized with barium carbonate, the solution filtered, reduced to small volume and cooled, when barium trifluoromethylfluoroborate crystallized as a hydrate. Drying *in vacuo* over phosphorus pentoxide gave the anhydrous salt, which was hygroscopic.

Anal. Calcd. for $Ba(CF_3BF_3)_2$: Ba, 33.4. Found: Ba, 33.4.

The infrared spectrum (KBr disc) showed absorptions at 637(m), 730(w), 963(s), 986(s), 1045(vs), 1065(vs), 1090(vs) cm.$^{-1}$.

Ammonium Trifluoromethylfluoroborate.—The free acid, prepared by passing a solution of the potassium salt through a cation exchange column, was neutralized with ammonium hydroxide and evaporated to dryness. The residue was dissolved in a little ethanol, filtered and the ethanol removed *in vacuo* to give ammonium trifluoromethylfluoroborate.

Anal. Calcd. for $NH_4BF_3CF_3$: N, 9.0. Found: N, 8.8.

The infrared spectrum (KBr disc) showed absorptions at 636(m), 731(w), 959(s), 984(s), 1043(vs), 1060(vs), 1085(vs), 1405(m), 2340(vw), 3060(w), 3180(m), 3440(w) cm.$^{-1}$.

Pyrolysis.—Potassium trifluoromethylfluoroborate (0.257 g., 1.46 mmoles) was heated *in vacuo* to 300°, when evolution of volatile material began. After maintaining at 330–350° for 30 min. decomposition appeared to be complete and volatile products were shown spectroscopically to be tetrafluoroethylene (0.065 g., 0.65 mmole, 89% yield) containing traces of silicon tetrafluoride and perfluorocyclopropane. The residual solid was shown spectroscopically to be potassium fluoroborate.

In another experiment potassium trifluoromethylfluoroborate (0.530 g., 3.00 mmoles) in an evacuated silica tube (10 ml.) was heated to 450° for 1 hr. At the end of this time some darkening had occurred and volatile products were found to be perfluorocyclobutane (0.121 g., 0.60 mmole, 80% yield) containing traces of silicon tetrafluoride and some fluoroölefins. Again, the residue was potassium fluoroborate.

Ammonium trifluoromethylfluoroborate (0.515 g., 3.32 mmoles) was heated to 150° *in vacuo*, when some decomposition began. At 175° rapid decomposition occurred and volatile products (0.164 g.) were shown spectroscopically to be mainly tetrafluoroethylene, with some fluoroform and silicon tetrafluoride. Spectroscopic examination of the solid residue showed that it was largely ammonium fluoroborate.

Hydrolysis.—Solutions of free trifluoromethylfluoroboric acid were prepared by passing solutions of the potassium salt (ca. 0.14 g.) in water (*ca.* 100 ml.) through a cation exchange column. Titration of the resulting acid showed that 1.02–1.04 equivalents of acid were produced for every mole of the potassium salt. The acid content of the solutions was unchanged on boiling for 3 hr.

Potassium trifluoromethylfluoroborate (0.221 g.) was boiled

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(10) D. M. Gage and E. F. Barker, *J. Chem. Phys.*, **7**, 455 (1939).

for 1 hr. with 10% sodium hydroxide solution (10 ml.). The solution was neutralized with sulfuric acid and evaporated to dryness and the solid extracted with ethanol, Evaporation of the ethanol gave solid material (0.098 g.) shown spectroscopically to be unchanged potassium trifluoromethylfluoroborate.

[CONTRIBUTION FROM THE THIOKOL CHEMICAL CORPORATION, REACTION MOTORS DIVISION, THIOKOL CHEMICAL CORPORATION, DENVILLE, NEW JERSEY]

Fluorination of Ammonia

BY SCOTT I. MORROW, DONALD D. PERRY, MURRAY S. COHEN AND CARL SCHOENFELDER

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The reaction of fluorine and ammonia was reinvestigated in packed copper reactors under varying conditions of stoichiometry. The results qualitatively confirmed the earlier work of Ruff for the reaction in which an excess of fluorine was employed, but in the present study the use of excess ammonia produced dinitrogen tetrafluoride, difluoramine and dinitrogen difluoride in addition to the previously obtained nitrogen trifluoride. The products were identified by infrared and mass spectrometric analysis. A mechanism for the reaction is suggested, which explains the formation of these products and is consistent with previously advanced fluorination mechanisms.

Introduction

The vapor phase reaction of ammonia and fluorine was originally investigated by Ruff and Hanke[1] in an unpacked T-shaped copper reactor with both an excess of fluorine and an excess of ammonia. The products in both cases were reported to be nitrogen trifluoride and ammonium fluoride (Equation 1), although the presence of other nitrogen fluorides was postulated. Yields of nitrogen trifluoride of about 6% were obtained,

$$4NH_3 + 3F_2 \longrightarrow NF_3 + 3NH_4F \qquad (1)$$

but the main reaction was evidently the formation of nitrogen and hydrogen fluoride (Equation 2). The latter then combined with unreacted ammonia to form ammonium fluoride (Equation 3).

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF \qquad (2)$$

$$HF + NH_3 \longrightarrow NH_4F \qquad (3)$$

We have reinvestigated this reaction to obtain more detailed information on reaction conditions, utilizing techniques such as the copper reactor packing of Fredenhagen and Cadenbach[2] and a reactor of modified design to supplement studies in the T-shaped reactor. The reaction was also explored under conditions which might be expected to yield difluoramine and monofluoroamine. Although difluoramine was first reported by Ruff and Staub,[3] recent work on its synthesis and characterization[4,5] has shown that the material described by the original authors was not difluoramine.

Our results not only confirmed those of Ruff and Hanke[1] on the preparation of nitrogen trifluoride but also showed that dinitrogen tetrafluoride, dinitrogen difluoride (difluorodiazine) and difluoramine can be obtained when an excess of ammonia is used. A preliminary report on the formation of dinitrogen tetrafluoride in this reaction has already been made.[6] Dinitrogen difluoride has previously been prepared by Haller,[7] and its structure has been determined by Bauer[8] and by Colburn, *et al.*[9]

Experimental

Reagents.—The fluorine used in this work was obtained from the Pennsalt Chemical Corporation, Philadelphia, Pennsylvania. Ammonia was supplied by the Matheson Company, East Rutherford, New Jersey. The Molecular Sieves were Linde Type 4-A, made by the Linde Company, Division of Union Carbide Corporation.

Apparatus.—A double valve system was used to control the flow of fluorine from the pressure storage cylinder. The gas was passed through a tube filled with sodium fluoride pellets to remove hydrogen fluoride impurity and thence through an orifice-type or glass, float-type flow meter to the reactor system. A stainless steel blowout manometer filled with fluorocarbon oil (Fluorolube, Hooker Electrochemical Company) was located in the fluorine feed line between the sodium fluoride tube and the flow meter. Fluorine was diluted with dry, oxygen-free nitrogen before entering the reactor. Ammonia was passed over a bed of soda lime and through a −23° trap to remove moisture, before it was diluted with nitrogen and fed into the reactor. When the T-shaped copper reactor was used, fluorine was introduced through the side arm and ammonia through the bottom port of the reactor. This reactor was made of a 12-inch section of two-inch diameter copper pipe, having a three-inch long side arm located four inches from the ammonia inlet. Figure 1 shows the method of introducing the gases into the homogeneous reactor. This reactor was made of a 36-inch length of two-inch diameter copper pipe. Copper gauze or copper shot was used for packing in both reactors. The temperature in the reaction zone was measured by means of a thermocouple inserted in a well in the side of the reactor. Effluent gases from the reactors were passed through −78° and −196° traps to recover products and unreacted ammonia. All of the connecting tubing in the reactor system was copper; the cold traps were machined from bar-stock Kel-F to fit standard stainless steel AN fittings. All of the valves were Hoke stainless steel needle valves. A burner filled with wood charcoal was situated in the exit line from the cold traps to convert fluorine to fluorocarbons when the apparatus was passivated by sweeping it with fluorine or when excess fluorine was used in the reaction.

Calibration of Fluorine Flow Meters.—The fluorine flow meters used in this work were calibrated by displacing nitrogen with fluorine from a long, narrow vertical copper tube. At low rates of flow for short periods of time no fluorine passed into the system in which the nitrogen was collected and measured. The amount of nitrogen displaced from the tube, measured by the displacement of water, gave a direct measure of the amount of fluorine passing through the meter.

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