pansion for pure nickel furnished by A. S. Friedman[4] of the National Bureau of Standards. The largest correction to the volume as the result of contraction of the pycnometer on cooling was 0.1911 cm.,[3] or 0.7% of its volume at 30°.

TABLE I

DENSITY OF LIQUID FLUORINE

T, °K.	Density, g./cm.^{3}	Dev. from eq. 1 Obsd. − calcd.	T, °K.	Density, g./cm.^{3}	Dev. from eq. 1 Obsd. − calcd.
65.78[a]	1.638	+0.004	86.91	1.496	+0.003
71.76	1.594	− .003	88.26[a]	1.481	− .002
74.93	1.578	+ .002	88.50	1.484	+ .002
78.59[a]	1.550	− .002	90.08	1.472	+ .002
78.62	1.553	+ .001	91.55[a]	1.458	− .001
81.72	1.532	+ .002	91.75	1.460	+ .003
81.73[a]	1.528	− .002	94.73[a]	1.434	.000
84.34	1.514	+ .003	97.56[a]	1.412	.000
85.05[a]	1.505	− .002	100.21[a]	1.391	.000
85.67	1.505	+ .003	102.75[a]	1.370	.000

[a] Indicates a separate run.

TABLE II

VALUES OF THE DENSITY OF LIQUID FLUORINE FROM VARIOUS SOURCES

Source	Temperature, °K. 66.00	77.16	85.02
Kanda[5]	1.173	1.130	...
Kilner, Randolph and Gillespie[6]	...	1.54	...
Elverum and Doescher[7]	1.636	1.567	1.510
White, Hu and Johnston[8]	1.634	1.563	1.513
This research	1.634	1.561	1.507

A comparison, at several temperatures, of the values for the density obtained in this study and those of various other sources are given in Table II. We agree well with White, Hu and Johnston[8] over the range duplicated and deviate only on extrapolation of their data to the boiling point of fluorine, 85.02°K.[9] Comparing with the data of Elverum and Doescher[7] we tend to parallel their data with their values being 0.2–0.3% higher.

The data of Table I have been fitted to the equation

$$d = 1.907 - 2.201 \times 10^{-3}T - 2.948 \times 10^{-5}T^2 \quad (1)$$

where d is the density in g./cm.^{3} at the absolute temperature T. Deviation between the experimental and values calculated from equation 1 are given in column 3 of Table I.

Acknowledgments.—The authors wish to express their thanks to Dr. J. F. Gall of the Pennsylvania Salt Manufacturing Company for his helpful interest, and to Dr. J. J. Fritz of the Pennsylvania State University for his advice during the course of this work. In addition the authors wish to express their appreciation to Dr. R. G. Ascah of the Pennsylvania State University for the thermometer calibration below 90°K., and to Mr. Gordon E. Webb of the Pennsylvania Salt Manufacturing Company for his excellent assistance.

---

[4] A. S. Friedman, private communication.

[5] E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 473 (1937).

[6] S. B. Kilner, G. L. Randolph, Jr., and R. W. Gillespie, THIS JOURNAL, **74**, 1086 (1952).

[7] G. W. Elverum and R. N. Doescher, *J. Chem. Phys.*, **20**, 1834 (1952).

[8] D. White, J. Hu and H. L. Johnston, THIS JOURNAL, **76**, 2584 (1954).

[9] J. Hu, D. White and H. L. Johnston, *ibid.*, **75**, 5642 (1953).

WYNDMOOR, PA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON AND THE UNIVERSITY OF NEW ENGLAND]

Pentafluorosulfur Hypofluorite and Thionyl Tetrafluoride

BY F. B. DUDLEY,[1] G. H. CADY AND D. F. EGGERS, JR.

RECEIVED OCTOBER 8, 1955

The silver difluoride "catalytic" fluorination of thionyl fluoride at 200° results in the formation of thionyl tetrafluoride, SOF_4, and a sulfur-hypofluorite-type molecule with the formula $SF_5{\cdot}OF$. The structure of each of these compounds has been confirmed by chemical reactions and by infrared spectra. In the vapor state, thionyl tetrafluoride absorbs strongly at 1383, 928, 821, 752, 637 and 567 cm.$^{-1}$, while the pentafluorosulfur hypofluorite absorption bands occur at 935, 888, 614 and 585 cm.$^{-1}$. Both substances are gases. Thionyl tetrafluoride condenses to give a colorless liquid boiling at −49.0° and freezing at −99.6°. Pentafluorosulfur hypofluorite condenses to form a faintly yellow liquid which freezes at −86.0° and boils at −35.1°. This substance is a highly reactive oxidizing agent with an odor like that of oxygen difluoride.

Introduction

The successful addition of fluorine to sulfur trioxide across a sulfur–oxygen double bond to form fluorine fluorosulfonate[2] suggested the possibility of forming other sulfur-hypofluorite-type molecules by allowing fluorine to react with molecules such as sulfur dioxide and thionyl fluoride. As expected, the predominant product of the reaction between fluorine and sulfur dioxide was sulfuryl fluoride, but a small amount of a highly reactive material of high molecular weight, and possessing the typical hypofluorite odor, indicated that a compound such as $SF_4(OF)_2$ or $SF_5(OF)$ was being formed. To test the first possibility, sulfuryl fluoride was passed through the silver difluoride "catalytic" reactor[3] with excess fluorine, but the sulfuryl fluoride was unchanged. If the reactive substance being sought had the structure SF_5OF, then the obvious preparative method would be the fluorination of thionyl fluoride. However, thionyl fluoride was known to react with fluorine on a platinum spiral at 150° to form thionyl tetrafluoride, SOF_4.[4] As a result of

---

[1] University of New England, Armidale, N. S. W., Australia.

[2] F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., THIS JOURNAL, **78**, 290 (1956).

[3] K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

[4] W. Kwasnik, F.I.A.T. Review of German Science (1939–46), Inorganic Chemistry, Vol. 1, 1948.

the stronger fluorinating conditions being employed in this research, further addition of fluorine was achieved, and two pure substances with the empirical formulas SOF_4 and SOF_6 were separated from the reaction products.

Preparations

Fluorination of Sulfur Dioxide.—A stream of nitrogen was bubbled through liquid sulfur dioxide, cooled in a Dewar flask above a Dry Ice–acetone mixture, and the gas mixture led into a previously described silver difluoride "catalytic" reactor heated to 200° where it mixed with a stream of fluorine gas also diluted with nitrogen. The gaseous mixture was then passed through traps cooled with liquid oxygen. The non-condensable gases were conveyed to the fume hood where they were regularly tested for fluorine, the flow rate of which was so adjusted that fluorine was kept in excess throughout the reaction.

Distillation of the 15 cc. of product indicated that it was essentially sulfuryl fluoride, 14 cc. distilling over in the temperature range −54.95 to −54.15°. Toward the end of the distillation with about 1 cc. of liquid left in the column, the temperature rose to −38.4°, and the last fraction was collected in the temperature range −38.4 to −35.5°. This latter fraction had a vapor density of 142 g. per g. mol. vol. It reacted rapidly with mercury and when treated with potassium iodide it liberated 1.57 equivalents of iodine per g. mol. vol. These properties suggested the possible presence of SOF_6 together with SO_2F_2.

Fluorination of Sulfuryl Fluoride.—The 14 cc. of sulfuryl fluoride collected in the previous distillation was slowly vaporized into a stream of nitrogen and was passed through the "catalytic" reactor at 200° together with excess fluorine. The entire product then distilled at −55.6°, and had a molecular weight of 102. The infrared spectrum and mass spectrogram agreed with those for sulfuryl fluoride.

Fluorination of Thionyl Fluoride.—A stream of nitrogen (10 liters per hour) was bubbled through liquid thionyl fluoride at −78°. This substance had been prepared using the procedure of Booth and Mericola[5a] as described by Martin.[5b] The vapor was swept by nitrogen into the silver difluoride "catalytic" reactor[3] heated to 200°, where it mixed with a stream of fluorine gas also diluted with nitrogen. The fluorine flow rate was so adjusted that fluorine was always present in excess. The reaction products were collected in traps cooled in liquid oxygen. Twenty-one g. of product was obtained from 16 g. of thionyl fluoride.

When this product was fractionally distilled in an analytical column of small volume the temperature rose gradually between −52 and −48°, indicating a poor separation of substances of nearly equal volatility. A larger and more efficient fractionating column was available. A larger sample (74 g.) of crude product was produced by fluorinating a 63-g. sample of thionyl fluoride. In both cases the crude product had a very striking bright yellow color similar to that obtained during the fluorination of sulfur dioxide. The yellow substance was not identified. Apparently it decomposes readily. A summary of the distillation results with the larger portion of crude product is given in Table I.

TABLE I

DISTILLATION OF PRODUCT OF FLUORINATION OF THIONYL FLUORIDE

Fraction	Wt.	Temp. range, °C.	Vapor density, g./G.M.V.
A	2.0	−52.3 to −50	109
B	1.2	−50 to −48.5	118
C	5.0	−48.5 to −47.8	120
D	11.0	−47.8 to −47.7	124
E	13.0	−47.7 to −47.0	128
F	3.0	−47.0 to −46.4	131
G	0.6	−46.4 to −46.2	133
H	1.2	−46.2 to −43.6	140
I	.6	−43.6 to −39.8	145
J	.4	−39.8 to −38.7	151
K	8.0	−38.7 to −36.0	162
L	8.8	−36.0 to −35.8	162
M	19.0	−35.8 to −35.6	162

Fractions D and E were combined and again fractionated. The purity of the fractions obtained was tested by infrared spectra. A progressive weakening of absorption bands at 1502 and 1269 cm.$^{-1}$ was observed on successive fractions. This indicated a contamination of the samples with sulfuryl fluoride, as other absorption bands of this molecule could also be detected.[6]

A 9.8-g. fraction was finally obtained in which the spectral absorption bands of sulfuryl fluoride were relatively insignificant. Analyses, reactions and determinations of physical properties were carried out on this material. This pure sample of thionyl tetrafluoride, SOF_4, represented only 13.2% of the total product. The bulk of the material, 48.4%, was a new and highly reactive material having the formula, SOF_6.

Apparatus.—Details concerning the apparatus employed for determining vapor pressure–temperature relationships,[3] melting points,[7] densities[2] and infrared spectra[1] are given in previous publications.

Analyses.—Each of the compounds was analyzed for sulfur and fluorine after hydrolysis with a potassium hydroxide solution. The alkaline solution was admitted to a bulb containing a weighed sample of gas. After the initial reaction, which was accompanied by fuming, the resulting solution was heated overnight on a steam-bath to ensure the complete hydrolysis of the fluorosulfonate ion originally formed. The solution was made up to 250 ml., and aliquots used for the analyses.

The sulfates were determined gravimetrically as barium sulfate. Additional aliquots were taken for the fluoride ion determination. The fluorine was steam distilled as fluorosilicic acid from a perchloric acid solution, and was then titrated with standard thorium nitrate solution using sodium alizarin sulfonate as indicator according to the procedure of Kimball and Tufts.[8] *Anal.* Calcd. for SOF_4: S, 25.9; F, 61.3. Found: S, 25.6, 25.6; F, 62.0, 62.1. Calcd. for SOF_6: S, 19.8; F, 70.4. Found: S, 19.8, 20.2; F, 71.1, 70.8.

Chemical Properties

Reactions of Thionyl Tetrafluoride.—As an aqueous cold neutral potassium iodide solution was admitted to a bulb containing a known weight of thionyl tetrafluoride, iodine flakes were at first liberated in large amount, but within a few seconds it was obvious that the free iodine was diminishing rather than increasing in quantity. The final solution was colorless. Apparently some of the thionyl tetrafluoride was at first reduced but the product in turn reduced free iodine. The solution became acidic during the reaction and gaseous sulfuryl fluoride remained in the bulb. In one case the production of hydrogen ion was 2.5 equivalents per mole of SOF_4 consumed and at the same time the volume of SO_2F_2 was 0.6 times the volume of SOF_4. The net reaction appeared to be a summation of the two changes

$$SOF_4 + H_2O = SO_2F_2 + 2HF$$

$$SOF_4 + 2H_2O = SO_3F^- + 3HF + H^+$$

As a cold solution of potassium hydroxide was admitted to a bulb containing thionyl tetrafluoride the gas reacted and dissolved leaving only a small gaseous residue. By titrating the resulting solution it was found that 3.9 equivalents of base had been consumed per mole of gas reacted. This is in accord with the equation

$$SOF_4 + 4OH^- = SO_3F^- + 2H_2O + 3F^-$$

---

(5) (a) H. S. Booth and F. C. Mericola, THIS JOURNAL, **62**, 640 (1940); (b) "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, Editor, J. C. Bailar, Jr., p. 133.

(6) W. D. Perkins and M. Kent Wilson, *J. Chem. Phys.*, **20**, 1791 (1952).

(7) L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).

(8) R. H. Kimball and L. E. Tufts *Anal. Chem.*, **19**, 150 (1947).

Reactions of Pentafluorosulfur Hypofluorite.—As a cold air-free neutral potassium iodide solution was introduced into a bulb containing a known weight of pentafluorosulfur hypofluorite, iodine was liberated freely. The volume of residual gas was approximately equal to that of the sample at the same temperature and pressure. The molecular weight and infrared spectrum of this residual gas showed it to be sulfuryl fluoride. Titration of the free iodine with sodium thiosulfate showed that 1.95 equivalents of iodine per mole had been liberated. The addition of potassium iodate and further titration with thiosulfate showed that 1.96 equivalents of hydrogen ion per mole had been formed. These facts are in accord with the equation

$$SOF_6 + 2I^- + H_2O = SO_2F_2 + 2HF + I_2 + 2F^-$$

The reaction of a known weight of pentafluorosulfur hypofluorite with a known quantity of potassium hydroxide resulted in strong fuming. The volume of residual gas, measured by water displacement was approximately equal to half the volume of the gas sample measured at the same temperature and pressure. The residual gas was oxygen. Titration of the unreacted alkali showed that 5.95 equivalents of hydrogen ion per mole had been produced by the reaction

$$SOF_6 + 6OH^- = {}^1/_2O_2 + 5F^- + 3H_2O + SO_3F^-$$

Physical Properties of Thionyl Tetrafluoride

Vapor Pressure and Boiling Point.—The temperature dependence of the vapor pressure in the temperature range 196.5 to 224.7°K. is given by the equation

$$\log_{10} P(\text{mm.}) = 7.2349 - \frac{8.5958 \times 10^2}{T} - \frac{2.6275 \times 10^4}{T^2}$$

where T is the temperature in degrees absolute. In Table II, the figures in parentheses were calculated from the above equation. The maximum deviation of observed pressures from calculated pressures is 0.6%. The vapor pressures calculated from the equation given by Kwasnik[4] are all higher than those observed in the present work and are not consistent with the boiling point reported.

TABLE II

VAPOR PRESSURES OF THIONYL TETRAFLUORIDE

T, °K.	P (mm.)	T, °K.	P (mm.)
(196.3)	(150)	(212.2)	(400)
196.5	151.4	213.5	428.7
197.4	160.3	215.6	481.5
198.6	174.3	217.7	538.8
(200.8)	(200)	219.4	593.1
202.7	225.1	(219.7)	(600)
205.2	264.4	221.1	642.9
207.1	296.3	(224.2)	(760)
211.2	378.4		

The boiling point at 760 mm., as obtained from the graph of log P(mm.) *versus* $1/T$, is −49.0°. Assuming ideal gas behavior, and using the Clapeyron equation, the latent heat of vaporization was calculated to be 5090 cal. per mole. This corresponds to a Trouton constant of 22.7.

Density.—The densities observed at −68.0, −64.3, −60.9 and −57.3° were 1.8525, 1.8372, 1.8234 and 1.8085 g. per cc., respectively. The temperature dependence of the density σ is given by the equation

$$\sigma_T = -4.1121 \times 10^{-3}T + 2.6963$$

The volume coefficient of expansion at −63°, calculated from the density values in Table III is −0.00224 per degree.

TABLE III

MASS SPECTRUM OF THIONYL TETRAFLUORIDE

Mass-charge ratio	Type of peak[a]	Relative intensities for ionizing voltage of 70 v.	Mass-charge ratio	Type of peak	Relative intensities for ionizing voltage of 70 v.
32	S	15.6	67	SOF	14.7
33.5	SOF, d	1.1	70	SF_2	14.5
35		1.4	86	SOF_2	22.7
43	SOF_2, d	2.1	89	SF_3	7.3
48	SO	8.3	105	SOF_3	100
51	SF	7.0	124	SOF_4	0.3

[a] d indicates doubly charged.

Melting Point.—The observed melting point of −99.6° was several degrees higher than the value −108° reported by Kwasnik.[4]

Molecular Weight.—Values obtained for the molecular weight ranged from 123.8 to 125.6 with an average value of 124.6 from six determinations.

Mass Spectrum.—The mass spectrum was recorded with a Consolidated Model 21-103 mass spectrometer. Table III indicates the relative abundance of the parent molecule ion and the more plentiful ionic species derived therefrom. In all cases where an ionic species was sufficiently plentiful, it was also possible to measure the heights of peaks corresponding to S_{33} and S_{34} isotopes which were present to the extent of approximately 1 and 4%, respectively.

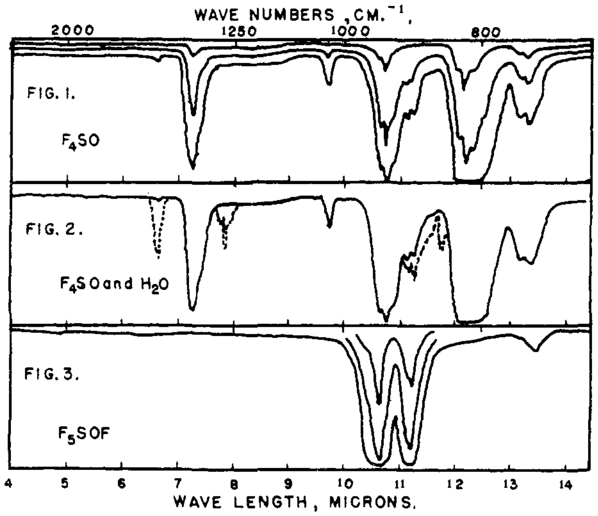
Infrared Spectrum.—The infrared spectrum obtained from thionyl tetrafluoride at 10.2 and 0.5 mm. in the rock salt region is reproduced in Fig. 1. The spectrum obtained in the KBr region at 10 mm. pressure is reproduced in Fig. 4. Strong absorption bands are centered at 1383, 928, 821, 752, 637 and 567 cm.$^{-1}$.

The separation of thionyl tetrafluoride from small amounts of sulfuryl fluoride is rather difficult. The relative purity of the sample finally obtained can be seen by the spectra reproduced in Fig. 1. The very weak peaks which can be observed at 1502 and 1269 cm.$^{-1}$ and the stronger peaks at 885 and 848 cm.$^{-1}$ are characteristic of the infrared spectrum of sulfuryl fluoride. The band at 1031 cm.$^{-1}$ is due to silicon tetrafluoride. The fact that thionyl tetrafluoride hydrolyzes to form sulfuryl fluoride is illustrated in Fig. 2. The heavy line represents the infrared spectrum at 10 mm. pressure. The dotted line, showing an increase in the intensity of the sulfuryl fluoride bands, was obtained with the same sample after the admission of a small amount of water vapor.

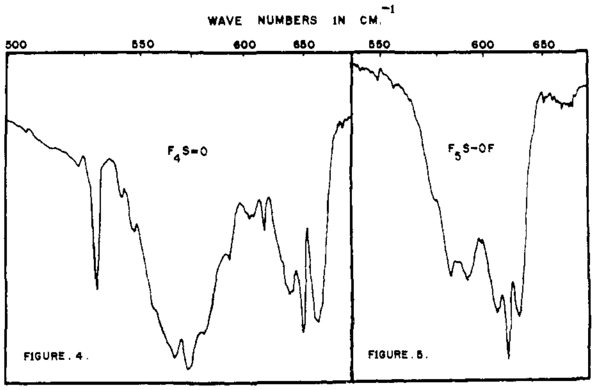
The band in the spectrum of thionyl tetrafluoride at 1383 cm.$^{-1}$ appears to be due to S=O stretch. This is consistent with the spectral frequency of 1333 cm.$^{-1}$ reported for the S=O stretch in thionyl fluoride.[9] Both these values are intermediate

---

(9) J. K. O'Loane and M. K. Wilson, *J. Chem. Phys.*, **23**, 1313 (1955).



Figs. 1, 2 and 3.—Infrared spectra in the NaCl region, using a 10-cm. cell at 25° in a Perkin-Elmer model 21 spectrometer; 1, SOF$_4$ at 10, 2 and 0.5 mm. pressure; 2, SOF$_4$ (solid line); after admission of water vapor (dotted line); 3, SOF$_6$ at 10, 2 and 0.5 mm. pressure.



Figs. 4 and 5.—Infrared spectra in the KBr region, using a 10-cm. cell at 25° in a modified Perkin-Elmer monochromator, model 99; 4, SOF$_4$ at 10 mm. pressure; 5, SOF$_6$ at 20 mm. pressure.

between the two S–O vibration frequencies reported for molecules containing two oxygen atoms doubly bonded to sulfur, as in sulfuryl fluoride, fluorine fluorosulfonate, etc. In the further assignment of observed bands of SOF$_4$, by comparison with SOF$_2$, it is instructive to compare the spectrum of SF$_4$ with that of SF$_6$. Upon increasing the number of fluorine atoms bonded to sulfur, the S–F stretching frequencies shift to higher values: from 738 and 723 cm.$^{-1}$ in SF$_4$ to 940 and 775 cm.$^{-1}$ in SF$_6$.[10] Thus we may expect, for SOF$_4$, values of the S–F stretching frequencies higher than the 808 and 748 cm.$^{-1}$ of SOF$_2$.[9] The very strong bands of SOF$_4$ at 928 and 821 cm.$^{-1}$ are then assigned to S–F stretching motions. The bending motions of SOF$_2$ occur at 530, 410 and 390 cm.$^{-1}$ [9]; we may surely assign the 567 cm.$^{-1}$ band of SOF$_4$ as a bending motion. The remaining two bands of SOF$_4$ at 752 and 637 cm.$^{-1}$ are weaker and more difficult to assign; they probably involve both bending and stretching of the S–F bonds.

Physical Properties of Pentafluorosulfur Hypofluorite

Vapor Pressure and Boiling Point.—The temperature dependence of its vapor pressure is given by the equation

$$\log_{10} P(\text{mm.}) = 6.03633 - \frac{4.2035 \times 10^2}{T} - \frac{7.836 \times 10^4}{T^2}$$

In Table IV, the figures in parentheses were calculated from the above equation. The deviation of experimentally observed vapor pressures from calculated values is less than 1% in the range 60 to 775 mm. The boiling point at atmospheric pressure, as obtained from the graph of $\log_{10} P$(mm). *versus* $1/T$, is −35.1°, and the heat of vaporization at this temperature, calculated from the Clapeyron equation and assuming ideal gas behavior, is 5210 cal. per mole. This corresponds to a Trouton constant of 21.9.

Table IV

Vapor Pressures of Pentafluorosulfur Hypofluorite

T, °K.	P (mm.)	T, °K.	P (mm.)
(191.3)	(50)	215.9	256
193.3	58.8	220.5	330.6
196.4	73.2	228.0	484
200.1	95.1	235.5	687.2
(200.8)	(100)	236.9	735
208	158.4	(237.7)	(760)
(211.7)	(200)	238.1	773.5

Density.—The densities observed at −64.3, −59.6, −55.7, −57.5 and −47.2° were 2.011, 1.995, 1.978, 1.963 and 1.947 g. per cc., respectively. The temperature dependence of the density σ is given by the equation

$$\sigma_T = -3.722 \times 10^{-3}T + 2.788$$

The volume coefficient of expansion at −56°, as calculated from the above densities is 0.001872 per degree.

Melting Point.—The observed melting point was −86.0°.

Infrared Spectrum.—The infrared spectrum of pentafluorosulfur hypofluorite in the rock-salt region at 10, 2 and 0.5 mm. is reproduced in Fig. 3, while Fig. 5 shows the spectrum obtained in the potassium bromide region at 20 mm. Strong absorption bands are centered at 935, 888, 614 and 585 cm.$^{-1}$. Remarkably few bands are present for a molecule containing eight atoms. There is, furthermore, no band at all which could be associated with S=O stretching. The scarcity of infrared bands indicates that the SF$_5$ group has been only slightly perturbed in the replacement of F by OF, and suggests that comparison with SF$_6$ might be helpful.

The band at 935 cm.$^{-1}$ is due to S–F stretching (940 cm.$^{-1}$ in both SF$_6$[10] and S$_2$F$_{10}$[11]). The band at 888 cm.$^{-1}$ is probably due to O–F stretching,[2] and the remaining bands due to motions combining stretching and bending of the S–F bonds, and stretching of the S–O bond.

Acknowledgment.—This work was performed

---

(10) R. T. Lagemann and E. A. Joues, *J. Chem. Phys.*, **19**, 534 (1951).

(11) D. Edelson, This Journal, **74**, 262 (1952).

under contract with the Atomic Energy Commission. One of us (D. F. E.) acknowledges support from the National Science Foundation.

SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

High Temperature Fluorination Reactions of Inorganic Substances with Bromine Trifluoride Addition Compounds[1a,1b]

BY IRVING SHEFT, ARTHUR F. MARTIN AND JOSEPH J. KATZ

RECEIVED JUNE 29, 1955

The addition compounds of BrF_3 with KF or SbF_5 are found to be excellent high temperature fluorinating agents. Dissociation pressures of $KBrF_4$ and BrF_2SbF_6 to 350° have been measured and are of such a magnitude that these reagents can be used even at 500° in closed reaction vessels without developing high pressures. Many inorganic compounds, including refractory oxides, feldspars and oxygen-containing salts which resist fluorination by BrF_3 itself are readily converted to fluorides and elemental oxygen by $KBrF_4$ and BrF_2SbF_6 at elevated temperatures. Apparatus and techniques for carrying out these unusual high temperature fluorination reactions are described and the relative merits of these two reagents compared on the basis of their acid–base relationship.

Introduction

Although numerous oxides or oxygen-containing compounds can be fluorinated smoothly with bromine trifluoride (b.p. 127°) in the liquid phase near room temperature,[2,3] there are many compounds which fail to react quantitatively or indeed to react at all with BrF_3 even at its boiling point. Certain of these, it is true, can be completely fluorinated with BrF_3 at temperatures of 200–300° and at pressures which are so high as to present formidable and at present intractable apparatus problems. Emeléus and co-workers[4,5] have described a number of addition compounds of BrF_3, in particular with KF and SbF_5, which appeared to present the possibility of utilizing the fluorinating capacity of BrF_3 at high temperature without the attendant disadvantages of high pressure. To this end the dissociation pressures of these two addition compounds have been measured and their capacity to function as fluorinating agents studied. We find that these compounds can be readily employed to temperatures of at least 500°, that they are exceedingly powerful and versatile reagents at elevated temperatures, and that in many respects $KBrF_4$ and BrF_2SbF_6 are by far the most convenient form in which fluorine can be utilized in the laboratory.

Experimental

Materials.—Bromine trifluoride (Harshaw Chemical Company) was purified from the main impurities which are bromine, bromine pentafluoride, hydrogen fluoride and nonvolatile metal fluorides by vacuum distillation; the fraction, b.p. 95–95.5° (250 mm.), was collected as a very pale yellow liquid and stored in a nickel vessel. The bromine trifluoride was again purified by distillation in the vacuum line just prior to use. Antimony pentafluoride was a commercial product obtained from the Harshaw Chemical Company and was used as received. The other chemicals in this work were of reagent grade and the standard feldspar sample was obtained from the National Bureau of Standards.

Preparation of BrF_2SbF_6 and $KBrF_4$.—The BrF_3–SbF_5 addition compound was prepared readily in quantity by dissolving SbF_5 in a 10% excess of BrF_3 in a nickel vessel. The excess BrF_3 was then removed from the solution by heating *in vacuo* at 130°. The identity of the product was established from the stoichiometry of the reaction. When pure, BrF_2SbF_6 is canary-colored; when prepared from commercial reagents, it is usually brick-red. BrF_2SbF_6 prepared as above is obtained as a free-flowing crystalline solid which is stable in dry air. Although the compound reacts vigorously with water, and will char or inflame moist cellulose, these reactions are very much more moderate than with liquid BrF_3 itself.

$KBrF_4$ can be prepared in exactly similar fashion by dissolving KF in a 10% excess of BrF_3 and removing the excess BrF_3 *in vacuo* at 130°. The addition compound is obtained as a free-flowing white crystalline powder, stable in dry air. In its reactions with water and various organic compounds it is distinctly less vigorous than BrF_2SbF_6.

The crystal structure of $KBrF_4$ was examined by Dr. Stanley Siegel. The symmetry of $KBrF_4$ is tetragonal with $a = 6.162$ kX. and $c = 11.081$ kX. The observed density leads to 4 molecules per unit cell with a calculated density $\rho = 3.06$ g./cm.^{3}. The space group is I4/mcm. The fluorine atoms are distributed in tetrahedral configurations about each bromine atom at a distance Br–F = 1.81 Å., which is close to the value (1.78 Å.) found in BrF_3 itself. The F–F distances within the BrF_4 group are 2.81 and 3.03 Å. Each potassium is bonded to 8 fluorine atoms with K–8F = 2.84 Å.

Dissociation Pressure Measurements.—Dissociation pressures were measured in an all-nickel apparatus which was placed in an air-thermostat. The temperature of the thermostat was maintained at 130° to prevent sublimation and condensation since it was found that no distillation of BrF_2SbF_6 occurred from the reaction zone when the cooler portions of the apparatus are maintained above 130°. The probable explanation for this behavior is that the vapor of BrF_2SbF_6 may be completely dissociated and recombination cannot occur in the absence of a liquid phase; the vapor pressures of the BrF_3 and SbF_5 themselves are such as to preclude their condensation. Pressures were measured through a Booth–Cromer[6] nickel diaphragm gage which was balanced by a precision mercury manometer.

Apparatus.—Nickel is usable with pure BrF_2SbF_6 and $KBrF_4$ up to a temperature of 500° and is therefore a suitable material of construction for high temperature fluorination apparatus. The dimensions of the nickel reaction tubes were $^3/_4'' \times 6''$ with an SAE $^3/_4''$ female flare at the top. The reaction tubes were attached by means of a $^3/_4''$ flare nut to a nickel block containing a Teflon-gasketed addition port through which the sample could be introduced; also attached to the nickel block (by means of silver solder) was a nickel diaphragm Hoke valve. The lower four-inch section of the reaction vessel was heated by an electric furnace; inserted into the furnace was a resistance thermometer which served as the sensing element for an electronic controller. The temperature cycle was followed

---

[1] (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission; (b) presented in part before the Division of Physical and Inorganic Chemistry at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

[2] H. J. Emeléus and A. A. Woolf, *J. Chem. Soc.*, 164 (1950).

[3] H. R. Hoekstra and J. J. Katz, *Anal. Chem.*, **25**, 1609 (1953).

[4] A. G. Sharpe and H. J. Emeléus, *J. Chem. Soc.*, 2135 (1948).

[5] A. A. Woolf and H. J. Emeléus, *ibid.*, 2865 (1949).

[6] S. Cromer, "The Electronic Pressure Transmitter and Self Balancing Relay," MDDC-803, 1949.