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N-Haliminosulfur Derivatives

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The compounds $O{=}SF_2{=}NCl$, $O{=}SF_2{=}NF$, and $SF_2{=}NCl$ were prepared by the catalytic halogenation of the corresponding N-fluoroformyl derivatives, $O{=}SF_2{=}NCOF$ and $SF_2{=}NCOF$. Some properties of these compounds are discussed.

The interaction of cesium fluoride with thionyl tetrafluoride and several other sulfur oxyfluoride derivatives containing a SO_2F group has been demonstrated.[1] The addition of cesium fluoride to the perfluoroalkyliminosulfur difluorides, $CF_3N{=}SF_2$ and $C_2F_5N{=}SF_2$, has been inferred from a study[2] of their fluorination products. This investigation extends the study of the effect of cesium fluoride on the imino derivatives $SF_2{=}NC({=}O)F$ and $O{=}SF_2{=}NCOF$. These materials were of particular interest since they contain two possible sites for nucleophilic attack by fluoride ion.

Results and Discussion

The $O{=}SF_2{=}N-$ System.—Several compounds containing the $O{=}SF_2{=}N-$ group have recently been prepared by the reaction of thionyl tetrafluoride with ammonia[3] or primary amines.[4] However, no examples were reported which contained another functional group in the molecule. Extension of the recently developed method for the formation of S–N double bonds to include SF_4O resulted in the preparation of N-fluoroformyliminosulfur oxydifluoride, OSF_2NCOF. Thionyl tetrafluoride was found to react with silicon tetraisocyanate in the presence of a small amount of boron trifluoride[5] to produce OSF_2NCOF in moderate yield.

$$Si(NCO)_4 + 4SF_4O \xrightarrow{BF_3} SiF_4 + 4OSF_2NCOF$$

N-Fluoroformyliminosulfur oxydifluoride is a colorless liquid which is stable in glass and is hydrolyzed slowly by water vapor.

Formulation of the product as N-fluoroformyliminosulfur oxydifluoride is based primarily on its infrared spectrum. A band characteristic of a COF group[6] as well as bands attributable to the asymmetric and symmetric stretching vibrations of the $O{=}S{=}N$ system[3,4] are present in the spectrum. In addition, the F^{19} nmr spectrum of the product shows that there are two types of fluorine present in the molecule in the expected 2:1 ratio. The mass cracking pattern of OSF_2NCOF also supports the presence of a COF group in the molecule since, in addition to containing a peak corresponding to the parent molecular ion, OSF_2NCOF^+, it contains a very strong peak due to the ion fragment, COF^+.

N-Fluoroformyliminosulfur oxydifluoride was found to be absorbed completely by excess cesium fluoride at ambient temperature. Decomposition of the mixture at 120–150° under vacuum produced an amount of carbonyl fluoride equivalent to the originally absorbed material. The reaction is believed to involve the nucleophillic attack of fluoride ion on the oxyfluoride. Since there are two sites for attack, carbon or sulfur, several different modes of reaction are possible (*e.g.*, addition of fluoride ion to form the ions of O^-SF_3NCOF or $OSF_2NCF_2O^-$ or cleavage to form the OSF_2N^- ion and COF_2).[7]

The addition of chlorine to the reactor containing OSF_2NCOF absorbed on cesium fluoride resulted in the formation of OSF_2NCl (the chlorination is more simply performed by allowing OSF_2NCOF and chlorine to react in the presence of excess cesium fluoride).

$$OSF_2NCOF + Cl_2 + F^- \longrightarrow OSF_2NCl + Cl^- + COF_2$$

N-Chloriminosulfur oxydifluoride is believed to arise from the chlorination of the OSF_2N^- ion (or perhaps the $OSF_2NCF_2O^-$ ion) since no reaction was observed between chlorine and OSF_2NCOF in the absence of cesium fluoride. Some further evidence for the existence of the OSF_2N^- ion has been obtained from a study of ammonia with thionyl tetrafluoride.[8] Fluorination of OSF_2NCOF in the presence of cesium fluoride produced a complex mixture. The desired compound, $O{=}SF_2{=}NF$, was obtained in low yield along with nitrogen trifluoride, carbonyl fluoride, and small amounts of thionyl fluoride and fluoroxytrifluoromethane. Variation in the reaction temperature (−25 to 25°) or in the mole ratio of reactants did not greatly effect the amount of product obtained.[9] N-Fluoriminosulfur oxydifluoride was also found to be absorbed by cesium fluoride, and this property was used to effect separation of the product from some of the impurities (*e.g.*, thionyl fluoride and starting material). Upon

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[1] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

[2] M. Lustig and J. K. Ruff, *ibid.*, **4**, 1444 (1965).

[3] R. Cramer and D. D. Coffman, *J. Org. Chem.*, **26**, 4010 (1961).

[4] G. W. Parshall, R. Cramer, and R. E. Foster, *Inorg. Chem.*, **1**, 677 (1962).

[5] Only trace amounts of product are obtained in the absence of boron trifluoride.

[6] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

[7] Under the reaction conditions any COF_2 liberated would be absorbed by the CsF to form $CsOCF_3$ [M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965)]. Heating the mixture to 120–150° results in the decomposition of $CsOCF_3$ to COF_2.

[8] F. Seel and G. Simon, *Angew. Chem.*, **72**, 709 (1960).

[9] N-Fluoriminosulfur oxydifluoride is difficult to handle, since it undergoes spontaneous and often explosive decomposition upon contact with air or upon shock. Therefore, caution should be exercised in working with this material.

heating the CsF–OSF_2NF adduct to 100°, N-fluoriminosulfur oxydifluoride could be recovered.

The infrared spectra of OSF_2NCl and OSF_2NF support their formulation as N-haliminosulfur oxydifluorides since both spectra contain bands attributable to the $O{=}SF_2{=}N$ group (*i.e.*, 1400 and 1120 cm^{-1} and 1409 and 1158 cm^{-1} for the NF and NCl compounds, respectively).[3,4] The F^{19} nmr spectrum of OSF_2NF contains two peaks (a doublet and a triplet) with the expected area ratio of 2:1. The larger peak is in the S–F region. Further support for the formulation of these materials as N-halo compounds is obtained from their mass cracking patterns. A large contribution to the pattern due to the molecular ion NX^+ is evident for both compounds. In fact, the NCl^+ peak is the strongest peak in the cracking pattern of OSF_2NCl. Both patterns also contain peaks due to the parent molecular ion. The ultraviolet spectrum of the chloro derivative contains a maximum at 231 mμ which is not present in the starting material and may arise from the presence of a N–Cl bond.[10]

The facile decomposition of OSF_2NF, though unexpected, suggested that OSF_2NCl might also undergo decomposition readily. This was found to occur. Ultraviolet irradiation of OSF_2NCl using light of wavelength 2537 A caused a complete and quantitative decomposition according to the equation

$$OSF_2NCl \longrightarrow SOF_2 + {}^1/_2N_2 + {}^1/_2Cl_2$$

On several occasions the spontaneous decomposition of OSF_2NF was controlled, which made it possible to analyze the products. They were found to consist of primarily thionyl fluoride, nitrogen, and fluorine. Thus, the mode of decomposition appears to be similar in both cases.

The $SF_2{=}N$– System.—N-Fluoroformylsulfur difluoride was reported to undergo decomposition at 190° to form carbonyl fluoride and thiazyl fluoride, FSN.[11] This decomposition has been found to be catalyzed by fluoride ion. Thus when cesium fluoride was employed, decomposition occurred at temperatures as low as 0°. The physical state of the cesium fluoride is an important factor in determining the procedure for isolation of the products. For example, if the reaction is carried out in a static reactor containing an excess of cesium fluoride which has been dried in the reactor (therefore caked), high yields of carbonyl fluoride and thiazyl fluoride can be removed from the reactor at ambient temperature. Alternately if the reactor, which contains stainless steel balls in addition to predried cesium fluoride, is shaken during the reaction, only a trace of the materials volatile at 25° is obtained. Upon heating this reactor to 100° under vacuum, good yields of carbonyl fluoride and thiazyl fluoride can be obtained. Under these experimental conditions either carbonyl fluoride or thiazyl fluoride itself is absorbed by excess cesium fluoride and may be regenerated in a similar manner.

The decomposition is believed to be a result of cleavage of SF_2NCOF by fluoride ion

$$SF_2NCOF + F \longrightarrow SF_2N^- + COF_2$$

$$SF_2N^- \rightleftarrows FSN + F^-$$

However, an apparent inconsistency exists. If the decomposition of SF_2NCOF proceeds through the formation of the SF_2N^- ion on the surface of cesium fluoride, why should this ion decompose to thiazyl fluoride and fluoride ion if the reactor is not shaken when thiazyl fluoride is absorbed by cesium fluoride during grinding? It is probable that there are sites on the surface of cesium fluoride which vary in their nucleophilic activity and that grinding increases the number of sites of high nucleophilicity. Since the initial attack of fluoride ion on SF_2NCOF is believed to occur on carbon rather than sulfur, it is not unreasonable to expect differences in the reactivity of thiazyl fluoride and SF_2NCOF toward nucleophiles. Thus, one surface site might be sufficiently active to decompose SF_2NCOF, but not active enough to stabilize the resultant SF_2N^- ion or to absorb the carbonyl fluoride produced. Grinding is therefore necessary to increase the number of active sites to accommodate the carbonyl fluoride and thiazyl fluoride. Further work will be necessary to confirm this speculation.

Thiazyl fluoride was found to react with chlorine in the presence of cesium fluoride to produce N-chloriminosulfur difluoride. The reaction could be performed either by allowing the two gaseous reactants to stand in the presence of cesium fluoride at 25° or by the interaction of chlorine with the preadsorbed FSN (presumably present as the F_2SN^- ion). However, the preparation of SF_2NCl is most conveniently carried out by the reaction of SF_2NCOF, cesium fluoride, and chlorine in a static system. The reactions occurring are felt to be identical with those discussed above, and this method has the advantage that it is not necessary to isolate thiazyl fluoride first. In the absence of cesium fluoride no reaction was observed between SF_2NCOF and chlorine, although thiazyl fluoride has been reported to react with chlorine in the gas phase to form thiazyl chloride.[12] Bromination of thiazyl fluoride in the presence of cesium fluoride produced an unstable material tentatively formulated as SF_2NBr on the basis of its infrared spectrum. A complete characterization was not attempted. During the preparation of SF_2NCl, a secondary reaction between SF_2NCl, cesium fluoride, and chlorine was observed which produced SF_5Cl and nitrogen. The amount of SF_5Cl formed became appreciable if the reactor was shaken during the reaction.

The structure of the product formed by the interaction of fluoride ion and thiazyl fluoride is not known. Both forms I and II probably contribute to the structure. Chlorination of these forms might be expected to occur on sulfur (form I) or on nitrogen (form II), thus

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[10] H. J. Emeléus and B. W. Tattershall, *Z. Anorg. Allgem. Chem.*, **327**, 147 (1964).

[11] A. F. Clifford, C. S. Kobayashi, and J. H. Stanton, Abstract of paper presented before the Symposium on Covalent Inorganic Fluorine Compounds, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1, 1964.

[12] O. Glemser and H. Richert, *Z. Anorg. Allgem. Chem.*, **307**, 313 (1961).

$^-SF_2{\equiv}N$ $F_2S{=}N^-$
I II

producing either $ClSF_2{=}N$ or $SF_2{=}NCl$. Thus, it is not immediately obvious which structure SF_2NCl has. The infrared spectrum of SF_2NCl is relatively simple in the rock salt region and contains strong bands at 1204, 744, and 687 cm^{-1}. The latter two bands are in the SF stretching region and are similar to those observed in the spectra of SF_2NCF_3 (759 and 716 cm^{-1}), SF_2NCOF (764 and 727 cm^{-1}), and SOF_2 (808 and 748 cm^{-1})[13] and are consistent with the presence of a $SF_2{=}$group. The remaining band is probably due to an S–N stretching mode. However, this stretching mode in compounds containing a S=N bond has been assigned[14] to a band occurring in the region of 1400 to 1350 cm^{-1} for several organo iminosulfur difluorides and in SF_2NCOF,[3] while the band attributed to the S≡N bond was found at 1515 cm^{-1} for both F_3SN[15] and $N{\equiv}SF_2N(C_2H_5)_2$.[16] Although the position of this band in the spectrum of SF_2NCl is not in agreement with either of the proposed structural assignments, additional evidence indicates the presence of a N–Cl bond in the product. Structures involving fluorine on both sulfur and nitrogen (*e.g.*, $SFCl{=}NF$ or FSNClF) are unlikely since only a single peak is observed in the F^{19} nmr spectrum of SF_2NCl. The ultraviolet spectrum of SF_2NCl contains a maximum at 242 mμ, while no such band is present in the spectra of $CF_3N{=}SF_2$, $SF_2{=}NCOF$, or $F_3S{=}N$. This band is perhaps attributable to a N–Cl bond.[12] Further support for the imino structure was obtained from the mass cracking pattern of SF_2NCl, since a peak due to the ion fragment $N^{35}Cl^+$ was observed. However, this evidence is not conclusive owing to the possibility of rearrangements in the ionization processes.

Several attempts were made to prepare N-fluoriminosulfur difluoride. Fluorination of thiazyl fluoride in the presence of cesium fluoride proceeded too far even at −78°. Only SF_5NF_2 and products derived from its cleavage with fluorine, SF_6 and NF_3, were formed in appreciable quantities. The action of silver difluoride on thiazyl fluoride or SF_2NCOF in a static system produced only thiazyl trifluoride in an essentially quantiative conversion.

$$2AgF_2 + FSN \xrightarrow{25^\circ} F_3SN + 2AgF$$

$$2AgF_2 + SF_2{=}NCOF \xrightarrow{25^\circ} F_3SN + COF_2 + 2AgF$$

The reaction of SF_2NCl with silver difluoride also failed to produce any of the desired material.

Experimental Section

Materials.—Thionyl tetrafluoride,[1] $SF_2{=}NCOF$,[17] and $Si(NCO)_4$[18] were prepared by the literature methods. The cesium fluoride was obtained from Penn Rare Metals, Inc., and dried overnight at 170–200° under high vacuum. This process resulted in caking of the cesium fluoride so it was removed to a nitrogen-filled drybox and finely ground before being loaded into prefluorinated metal reactors.

Analysis.—The analysis of gaseous mixtures was performed with the aid of a mass spectrometer which had been calibrated with the pure components of the mixture. The fluorine content of the samples was determined by titration of the fluoride ion formed by hydrolysis of the sample with 30% aqueous KOH at 100° for 12–15 hr. Nitrogen was determined by the Dumas method.

Nmr Spectra.—The F^{19} nmr spectra of the new materials prepared in this investigation were obtained on CCl_3F solutions with a Varian Model V4310A spectrometer operating at 40 Mc. Trichlorofluoromethane was used as an internal standard. The values for the chemical shift are given in ϕ units which are ppm relative to CCl_3F.

Ultraviolet Spectra.—The ultraviolet spectra of the new compounds prepared in this investigation and some previously reported compounds were obtained on gaseous samples using a Beckman DKU spectrophotometer.

Infrared Spectra.—The infrared spectra of all the compounds were taken with a Perkin-Elmer Model 521 spectrophotometer using a cell equipped with silver chloride windows. The observed bands are tabulated in Table I.

TABLE I

INFRARED SPECTRA OF THE IMINOSULFUR DERIVATIVES (CM^{-1})

OSF_2NCl	OSF_2NF	OSF_2NCOF	$SF_2{=}NCl$
1409 vs	1400 vs	2201 w	1280 w
1158 vs	1120 vs	2060 w	1204 sh
821 vs	1043 w	1868 m, sh	1189 s
670 w	843 vs	1823 vs	810 w
547 m (triplet)	777 s	1433 vs	744 vs
	563 m (triplet)	1303 sh	687 vs
	500 w	1276 vs	642 w
		1164 m	553 m
		1112 w	546 m
		911 s	
		870 s	
		811 m	
		787 m	
		763 m	
		583 ms	

Mass Spectra.—The mass spectra of the compounds were obtained with a Consolidated Engineering Corp. Model 21-260 spectrometer operating with an ionization voltage of 100 v.

Preparation and Characterization of $O{=}SF_2{=}NCOF$.—A 2.81-g (14.3 mmoles) sample of $Si(NCO)_4$ was loaded into a 150-ml monel Hoke cylinder in a drybox. Thionyl tetrafluoride, 8.70 g (70.2 mmoles), and BF_3, 8.02 mmoles, were condensed into the bomb. It was then heated at 235–240° for 3 hr. The reaction mixture was fractionated through −64, −95, and −196° cold baths. The −95° trap contained 4.05 g of crude product which was contaminated with approximately 4% SiF_3NCO (by mass spectral analysis). For most of the reactions which were carried out with $O{=}SF_2{=}NCOF$, the purity of the crude product was satisfactory. The isocyanate impurity could be removed by selective hydrolysis. For example, a 2.62-g sample of the above crude product was condensed onto 20 g of NaF to which 20 μl of H_2O had been added. The mixture was allowed to stand for 0.5 hr. A 1.79-g sample of pure $O{=}SF_2{=}NCOF$ was obtained by refractionation; bp 39°.

Anal. Calcd for OSF_2NCOF: N, 9.52; F, 38.8; mol wt, 147. Found: N, 9.38, F, 38.1; mol wt (vapor density), 145, 144.

The F^{19} nmr spectrum of $O{=}SF_2{=}NCOF$ consists of a doublet centered at ϕ −46.0 and a broad band at ϕ −15.8 (area ratio 2.07:1, respectively). Upon cooling to −95° the broad band resolves into a triplet; $J_{FF} \doteq 10$ cps. Homonuclear decoupling experiments showed that the fluorines at ϕ −46.0 are coupled

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[13] J. K. O'Loare and M. K. Wilson, *J. Chem. Phys.*, **23**, 1313 (1955).

[14] W. E. Smith, C. W. Tullock, R. N. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 551 (1960).

[15] H. Richert and O. Glemser, *Z. Anorg. Allgem. Chem.*, **307**, 328 (1961).

[16] O. Glemser, H. Meyer, and A. Haas, *Ber.*, **98**, 2049 (1965).

[17] A. F. Clifford and C. S. Kobayashi, *Inorg. Chem.*, **4**, 571 (1965).

[18] J. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **62**, 761 (1940).

to the fluorine at ϕ −15.8 since irradiation of the latter peak resulted in the collapse of the doublet. The infrared spectrum of OSF_2NCOF is given in Table I. Only a weak band at 261 μ ($\epsilon \sim 3$) was found in the ultraviolet spectrum of OSF_2NCOF. The mass spectrum of OSF_2NCOF contained the following, given as mass number, molecular ion assignment, and relative abundance: 147, OSF_2NCOF^+, 57%; 128, OSF_2NCO^+, 77%; 86, SOF_2^+, 16%; 67, SOF^+, 54%; 48, SO^+, 10%; 47, COF^+, 100%; 46, SN^+, 9%; 42, NCO^+, 37%; 32, S^+ (O_2^+), 14%; and 28, CO^+, N_2^+, 25%.

Preparation and Characterization of $O{=}SF_2{=}NCl$.—A 3.05-mmole sample of crude (96% purity) $O{=}SF_2{=}NCOF$ and 3.34 mmoles of chlorine were condensed into a 150-ml monel Hoke cylinder which contained 10 g of dried CsF and approximately 30 $^3/_8$-in. stainless steel balls. The bomb was placed on a wrist-action shaker and shaken for 4 hr at 25°. The crude product, 3.51 mmoles, was removed from the reactor at 25° and then fractionated through −78, −126, and −196° cold baths. The −196° trap contained Cl_2 (0.31 mmole), SO_2F_2 (0.05 mmole), SiF_4 (0.15 mmole), and CO_2 (0.03 mmole). The −126° trap contained essentially pure (99%) $O{=}SF_2{=}NCl$ (3.02 mmoles). The reactor was heated to 150° under vacuum and 2.95 mmoles of COF_2 was obtained. Alternately the combined crude product from several runs could be purified by low-temperature distillation; bp 19.8°.

Anal. Calcd for OSF_2NCl: N, 10.33; F, 28.0; Cl, 26.2; mol wt, 135.5. Found: N, 10.11; F, 27.4; Cl, 25.8; mol wt (vapor density), 134, 137.

The F^{19} nmr spectrum of OSF_2NCl contains a single band at ϕ −43.0 while the ultraviolet spectrum of this material has a maximum at 231 mμ (ϵ 228). The mass spectrum of OSF_2NCl contained the following, given as mass number, molecular ion assignment, and relative abundance: 135, OSF_2NCl^{35+}, 23%; 100, OSF_2N^+, 17%; 86, SOF_2^+, 7%; 67, SOF^+, 23%; 51, $N^{37}Cl^+$, 34%; and 49, $N^{35}Cl^+$, 100%.

Preparation and Characterization of $O{=}SF_2{=}NF$.—A 1.06-mmole sample of $O{=}SF_2{=}NCOF$ was condensed into a 75-ml monel pressure reactor containing 5 g of dried CsF. Fluorine, 2.13 mmoles, was expanded into the reactor at −196°. The reactor was then quickly warmed to ambient temperature and allowed to stand for 1 hr. The product mixture was transferred from the bomb and any unreacted fluorine was pumped off through a KOH trap. Fractionation of the mixture through −78, −126, and −196° cold baths gave the following product distribution: the −126° bath contained $O{=}SF_2{=}NF$ (0.25 mmole), SOF_2 (0.08 mmole), and $O{=}SF_2{=}NCOF$ (0.07 mmole). The −196° trap contained NF_3 (0.46 mmole), COF_2 (0.32 mmole), and CF_3OF (0.09 mmole). The crude product, 2.23 mmoles (obtained from the −126° trap after fractionation), from six runs was combined and condensed into a 150-ml monel bomb containing 10 g of dried CsF and approximately 30 $^3/_8$-in. stainless steel balls. The reactor was shaken for 1 hr before removing the material volatile at 25°. Thionyl fluoride (0.41 mmole) and SO_2F_2 (0.04 mmole) were obtained. The product was removed from the reactor by distillation at 80° under vacuum and was purified by refractionation through a −126° cold bath to remove the small amount of COF_2 arising from the thermal decomposition of $CsOCF_3$.

Anal. Calcd for OSF_2NF: F, 31.9; N, 11.76; mol wt, 119. Found: F, 31.2; N, 11.50; mol wt (vapor density), 117, 118.

Caution!—The fluorimine, OSF_2NF, will explode on contact with air. It has also undergone spontaneous decomposition during vacuum line handling or during shaking in the CsF bomb on numerous occasions.

The F^{19} nmr spectrum of OSF_2NF contained a doublet at ϕ −37.3 and a triplet at ϕ 113.1 (J_{FF} = 24 cps) with a relative area ratio of 1.94:1.00. The mass spectrum of OSF_2NF contained the following, given as mass number, molecular ion assignment, and relative abundance: 119, OSF_2NF^+, 57%; 100, OSF_2N^+, 6%; 86, SOF_2^+, 78%; 70, SF_2^+, 15%; 67, SFO^+, 100%; 51, SF^+, 8%; 48, SO^+, 13%; 33, NF^+, 42%; and 32, S^+ (O_2^+), 16%.

Preparation and Characterization of $SF_2{=}NCl$. Method A.—A 2.07-mmole sample of $SF_2{=}NCOF$ and Cl_2, 2.21 mmoles, were condensed into a 150-ml monel Hoke cylinder containing 5 g of dried CsF. The reactor was allowed to warm to ambient temperature and to stand for 3 hr without shaking. The reaction mixture was fractionated through −78, −126, and −196° cold baths. The −196° trap contained 1.82 mmoles of COF_2, 0.11 mmole of CO_2, and 0.12 mmole of Cl_2. The product, 2.01 mmoles, was found in the −126° trap. It was contaminated with approximately 0.04 mmole of SO_2. The combined product fraction from several runs was purified by low-temperature distillation; bp 24.1°.

Method B.—The procedure described above was repeated using 1.03 mmoles of FSN and 1.13 mmoles of Cl_2. A yield of 0.97 mmole of SF_2NCl was achieved following an identical purification procedure.

Anal. Calcd for SF_2NCl: N, 11.72; Cl, 29.7; S, 26.8; F, 31.8; mol wt, 119.5. Found: N 11.25; Cl, 29.2; S, 27.1; F, 30.1; mol wt, (vapor density), 117, 119.

The F^{19} nmr spectrum of SF_2NCl consists of a single band at ϕ −46.3, while the ultraviolet spectrum contains a maximum at 242 mμ (ϵ 134). The ultraviolet spectrum of F_3SN showed only end absorption beginning at 220 mμ. The mass cracking pattern of SF_2NCl consisted of the following, given as mass number, molecular ion assignment, and relative abundance: 121, $F_2SN^{37}Cl^+$, 30%; 119, $F_2SN^{35}Cl^+$, 86%; 100, $FSN^{35}Cl^+$, 10%; 84, SF_2N^+, 28%; 70, SF_2^+, 100%; 65, FSN^+, 24%; 51, SF^+ ($N^{37}Cl$), 12%; 49, $N^{35}Cl^+$, 14%; 46, SN^+, 16%; 35, $^{35}Cl^+$, 15%; and 32, S^+, 7%.

Reaction of $SF_2{=}NCOF$ with CsF. Case A.—A sample of $SF_2{=}NCOF$, 2.01 mmoles, was condensed into a 150-ml monel Hoke cylinder containing 5 g of dried CsF. The mixture was maintained for 3 hr at 25° before being fractionated through −78, −126, and −196° cold baths. Carbonyl fluoride, 1.67 mmoles, was found in the −196° trap and FSN, 1.81 mmoles, was obtained from the −126° trap. A small amount of SO_2, 0.07 mmole, was also found in the latter trap. The FSN was identified by infrared and vapor density molecular weight (found 63, 62; calcd 65).

Case B.—The above reaction was repeated by condensing 3.12 mmoles of $SF_2{=}NCOF$ into a 150-ml monel Hoke cylinder which contained approximately 30 $^3/_8$-in. stainless steel balls in addition to 10 g of CsF. After warming to ambient temperature the mixture was shaken for 3 hr. Only a trace amount of volatile materials could be removed from the reactor under vacuum at 25°. However, heating the reactor under vacuum to 120–130° yielded a mixture of COF_2, 3.01 mmoles, and FSN, 2.89 mmoles, together with small amounts of SO_2, 0.11 mmole, SO_2F_2, 0.10 mmole, and CO_2, 0.07 mmole.

Reaction of FSN with CsF.—A 4.23-mmole sample of FSN was condensed into a 150-ml monel Hoke bomb containing 10 g of CsF and approximately 30 $^3/_8$-in. stainless steel balls. The mixture was warmed to ambient temperature and shaken for 3 hr. Only a trace amount of volatile material could be removed from the bomb at 25°. However, a recovery of 4.19 mmoles of FSN was made by pumping on the reactor at 125° under vacuum.

Reaction of FSN with Br_2 in the Presence of CsF.—A mixture of FSN, 3.81 mmoles, and Br_2, 2.48 mmoles, was condensed into a 150-ml monel Hoke bomb containing 5 g of CsF. The mixture was allowed to stand for 3 hr before being fractionated through −95 and −196° cold baths. A 1.30-mmole sample of FSN contaminated with a small amount of SO_2 was found in the −196° trap. The −95° trap contained 2.33 mmoles of an unstable material which upon standing in glass gave bromine, SO_2, SiF_4, and FSN. Its infrared spectrum contained bands at 1215 (s), 1179 (w), 743 (vs), and 685 (s) cm^{-1}.

Reaction of $F_2S{=}NCl$ with Cl_2 in the Presence of CsF.—A 2.63-mmole sample of $F_2S{=}NCl$ and 6.02 mmoles of Cl_2 were condensed into a 150-ml monel bomb containing 10 g of CsF and approximately 30 $^3/_8$-in. stainless steel balls. The mixture was shaken for 8 hr at 25°. The crude product, 6.63 mmoles, was found to consist of N_2 (0.95 mmole), SF_2=NCl (0.69 mmole), SF_5Cl (1.80 mmoles), and Cl_2 (4.19 mmoles) by mass spectral analysis. Under similar reaction conditions SF_4 was completely converted to SF_5Cl by Cl_2 in the presence of CsF.

Decomposition Studies. A.—The photolytic decomposition of O=SF_2=NCl was studied by irradiating a 4.08-mmole sample of O=SF_2=NCl for 2 hr with a Hanovia lamp (Model 88A45). The crude mixture, 8.19 mmoles, consisted of 4.05 mmoles of SOF_2, 2.08 mmoles of N_2, and 2.06 mmoles of Cl_2. The related material, OSF_2NCOF, underwent no decomposition under these conditions.

B.—A 3.71-mmole sample of SF_2=NCl was irradiated for 1 hr under the same conditions as above. The crude mixture contained Cl_2 (1.90 mmoles), N_2 (1.57 mmoles), SF_4 (1.32 mmoles), SOF_2 (0.61 mmole), FSN (0.32 mmole), and SiF_4 (0.36 mmole). A solid deposit was left in the reactor which was not soluble in water.

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The Reaction of Antimony(V) Fluoride with Tetrafluorohydrazine and Difluorodiazine[1]

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The reaction of SbF_5 with N_2F_4 and N_2F_2 produced the two adducts $N_2F_4\cdot 2SbF_5$ and $N_2F_2\cdot 2SbF_5$, respectively. Some of their reactions as well as their possible structures are discussed.

Antimony(V) fluoride is known to form complexes with a large number of fluorides. The alkali metal fluorides as well as other metallic fluorides form simple ionic salts containing the hexafluoroantimonate anion. Several nonmetal fluorides such as SF_4, SF_4O, BrF_3, and AsF_3 also form complexes with antimony(V) fluoride. Their structure, however, has not definitely been established, although some evidence for an ionic composition has been advanced.[2] A discussion of the complexes formed between antimony(V) fluoride and several nonmetal fluorides has been presented recently.[3] Since *cis*-difluorodiazine was reported to form fluorodiazonium hexafluoroarsenate when treated with arsenic(V) fluoride,[4] it was of interest to investigate the interaction of antimony(V) fluoride with difluorodiazine and tetrafluorohydrazine.

Experimental Section

Preparation of NF_2SbF_5 and $NF_2(SbF_5)_{1.5}$.—A mixture of 2.15 g of $AsF_3\cdot SbF_5$ in 10 ml of AsF_3 was allowed to react with excess N_2F_4 (at a partial pressure of <100 mm) at −10° for 2.5 hr. After consumption of N_2F_4 ceased, the solvent and excess N_2F_4 were removed under vacuum and then fractionated. The residue was pumped on at 40–45° until it reached constant weight; mp 74–78°. The weight of product formed was 1.880 g (calculated weight based on the N_2F_4 consumed 1.870 g).

Anal. Calcd for $N_2Sb_3F_{19}$: Sb, 48.5; N, 3.71. Found: Sb, 48.1; N, 3.56; Sb/N, 1.55.

The above procedure and reaction temperature was repeated in a glass pressure vessel using 1.96 g of AsF_3SbF_5 in 10 ml of AsF_3 and excess N_2F_4 ($P_{N_2F_4} < 2$ atm). After consumption of the N_2F_4 ceased, the reaction mixture was treated as before. The residue was pumped on at 40–45° until it reached constant weight; mp 116–119°. The weight of product formed was 1.492 g (calculated weight based on the N_2F_4 consumed 1.526 g).

Anal. Calcd for NF_2SbF_5: N, 5.20; Sb, 45.4. Found: N, 5.23, 5.28; Sb, 44.9, 45.2.

A 0.612-g sample of NF_2SbF_5 was placed in a glass trap and approximately 2 ml of SbF_5 was condensed into the trap. The mixture was allowed to warm to ambient temperature and was stirred for 15 min. The excess SbF_5 was removed and the residue pumped on at 40–45° until it reached a constant weight of 0.851 g (calculated weight for $N_2F_4\cdot 3SbF_5$ 0.860 g); mp 75–77°. A mixture melting point with a sample of $N_2F_4\cdot 3SbF_5$ prepared as described above showed no depression. The complex $NF_2(SbF_5)_{1.5}$ could be converted to NF_2SbF_5 either by its reaction with N_2F_4 at $P_{N_2F_4} > 2$ atm as described above or by extraction with sulfur dioxide for 15 min at −65°.

Preparation of $NFSbF_5$.—Approximately a 2-g sample of SbF_5 was condensed onto the walls of a U tube. Then the system was pressurized to 300–400 mm of N_2F_2 (either the *trans* or the *cis* isomer could be used). The SbF_5 was allowed to melt and then a 40–50° water bath was placed around the U tube. When the consumption of N_2F_2 was nearly complete, the excess was removed and its amount determined. The residue was pumped on until it reached a constant weight of 1.592 g (calculated weight based on the N_2F_2 consumed 1.567 g); mp 82–84°.

Anal. Calcd for $NFSbF_5$: N, 5.60; Sb, 48.8. Found: N, 5.51; Sb, 48.6, 48.7.

Thermal Decomposition of NF_2SbF_5 and $NFSbF_5$.—A 0.6275-g sample of NF_2SbF_5 was placed in a U tube in a drybox. The U tube was then attached to a fractionation train on a standard vacuum line and evacuated. A 2.516-g sample of KF was placed in an adjacent U tube and this was cooled to −78°. A −196° bath was placed around the next U tube. While the system was pumped on, a 200° oil bath was raised around the U tube containing the sample and kept there for 15 min. The contents of the cold traps were then analyzed. Tetrafluorohydrazine, 1.12 mmoles of 97% purity, was obtained in the

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