$$\mathrm{Si_2H_6} \underset{k_T}{\overset{k_I}{\rightleftharpoons}} 2\mathrm{SiH_3} \tag{7}$$

$$k_I(\mathrm{Si_2H_6}) = k_T(\mathrm{SiH_3})^2$$

With *A* factors from the ethane[6] pyrolysis and a value for the silicon–silicon bond energy, one can estimate the silyl radical concentration. With $D(\mathrm{H_3Si{-}SiH_3}) = 58$, 67, and 81 kcal/mol, the silyl radical concentrations are 10^{-8}, 10^{-10}, and 10^{-13} *M*, respectively. The silicon–silicon bond energy in disilane is open to some question. From heats of formation data a value of 46 kcal/mol has been obtained.[8] However, it has been demonstrated that the silicon–hydrogen bonds in disilane are probably weaker than those in silane.[9] This result would somewhat increase the silicon–silicon bond strength calculated by Gunn and Green. A recent kinetic study has set the silicon–silicon bond energy in hexamethyldisilane at 67 kcal/mol.[10] From both steric arguments and predicted changes in hybridization, one would expect $D(\mathrm{SiH_3{-}SiH_3}) > D((\mathrm{CH_3})_3\mathrm{Si{-}Si}(\mathrm{CH_3})_3)$. A direct measurement by electron impact has set $D(\mathrm{H_3Si{-}SiH_3})$ at 81 ± 4 kcal/mol.[11] This latter value is in agreement with a value for $D(\mathrm{SiH_3{-}H})$ of 94 kcal/mol obtained both from electron impact studies on silane[12] and from an observation that silyl abstracts hydrogen from toluene at an appreciable rate.[13] Therefore, if $D(\mathrm{H_3Si{-}SiH_3})$ is at least 67 kcal/mol, which appears to be the case, then the fact that tetrasilane was not obtained in the disilane pyrolysis argues against our route B and therefore is in favor of our route A.

The pyrolysis of trisilane is slightly more complex. Since the trisilane pyrolyses were carried out at temperatures below which disilane did not decompose, it is unlikely that the silane was derived from secondary pyrolysis of disilane.

It would be difficult to calculate with any certainty the relative radical concentrations for this system so it is difficult to determine whether the apparent nonobservation of penta- and hexasilane is significant. If this point is significant, it would also argue against silyl-type radicals. Our results from the pyrolysis of trisilane can be explained by

$$\mathrm{Si_3H_8} \longrightarrow \mathrm{SiH_2} + \mathrm{Si_2H_6} \tag{8}$$

$$\mathrm{Si_3H_8} \longrightarrow 2\mathrm{SiH_2} + \mathrm{SiH_4} \tag{9}$$

$$\mathrm{SiH_2} + \mathrm{Si_3H_8} \longrightarrow \mathrm{Si_4H_{10}} \tag{10}$$

The results obtained from the pyrolyses over a Pyrex surface demonstrate that these reactions are catalyzed by Pyrex. Purnell and Walsh have demonstrated[14] that the pyrolysis of silane is catalyzed by Pyrex but is homogeneous over a silicon mirror. It is also of interest that they favor hydrogen elimination as the first step in the pyrolysis of silane

$$\mathrm{SiH_4} \longrightarrow \mathrm{SiH_2} + \mathrm{H_2} \tag{11}$$

Acknowledgment.—The authors are indebted to Dr. H. E. O'Neal for discussions on kinetics and to the Army Research Office (Durham) for financial support.

---

[8] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

[9] R. P. Hollandsworth and M. A. Ring, *Inorg. Chem.*, **7**, 1635 (1968).

[10] I. M. T. Davidson and I. L. Stephanson, *J. Chem. Soc.*, *A*, 282 (1968).

[11] W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962).

[12] W. C. Steele, L. D. Nichols and F. G. A. Stone, *ibid.*, **84**, 441 (1962).

[13] H. E. O'Neal, private communication, 1968.

[14] J. H. Purnell and R. Walsh, *Proc. Roy. Soc.*, **A293**, 543 (1966).

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute, Blacksburg, Virginia

Reactions of Pentafluorosulfanylamine and Pentafluorosulfanyliminosulfur Difluoride[1]

By Alan F. Clifford and Gerald R. Zeilenga

Received December 26, 1968

In recent years, considerable interest has been shown in nitrogen–sulfur–fluorine compounds. The compounds $\mathrm{SF_5NH_2}$, prepared by the reaction of $\mathrm{NSF_3}$ and HF,[2] and $\mathrm{SF_5N{=}SF_2}$, obtained in low yield either from $\mathrm{SF_4}$ and $\mathrm{NSF_3}$ using a $\mathrm{BF_3}$ catalyst[3] or from the fluorination of $\mathrm{S_4N_4}$,[4] have recently been reported. The purpose of this work was to examine some of the reactions of $\mathrm{SF_5NH_2}$ and $\mathrm{SF_5N{=}SF_2}$ in an attempt to prepare new pentafluorosulfanyl-nitrogen compounds.

Experimental Section

Apparatus.—Reactions were carried out in 75-ml Hoke stainless steel cylinders equipped with Hoke 300 series needle valves. An all-glass high-vacuum system was used for measurement, handling, and purification of volatile materials. All vacuum stopcocks and other joints were lubricated with Kel-F Brand No. 90 grease. An auxiliary system constructed with copper tubing and a manometer of Kel-F tubing was used for handling HF. Metal-to-glass connections were made with Swagelok (Crawford Fitting Co., Cleveland, Ohio) fittings equipped with Teflon ferrules.

The infrared spectrum of $(\mathrm{SF_5N{=}})_2\mathrm{SF_2}$ was obtained in the 2–15-μ region using a Perkin-Elmer Model 137 Infracord spectrometer. In the 11–25-μ region a Beckman IR5A spectrometer equipped with CsBr optics was employed. Pyrex 10-cm gas cells were used, fitted with NaCl windows for the 500–700-cm^{-1} region and KBr windows for the 900–400-cm^{-1} region.

Materials.—Sulfur tetrafluoride (Matheson) was used without further purification, since thionyl fluoride was the only impurity observed in the infrared spectrum. Hydrogen fluoride (Blockson Chemical Division of Olin Mathieson), silver(II) fluoride (Harshaw, technical grade), phosphorus pentafluoride (Matheson), and boron trifluoride (Matheson) were also used without purification. Cesium fluoride (American Potash and Chemical Corp.) was treated with fluorine at 110° for 1 hr to remove chloride and carbonate impurities. Fluorine (General Chemical Division of Allied Chemical) was passed over sodium fluoride pellets before use to remove HF. Sodium fluoride pellets (Harshaw) were heated under vacuum to dry them. Fluoroformyliminosulfur difluoride, $\mathrm{F_2S{=}NCOF}$, was prepared by the reaction of silicon tetraisocyanate and sulfur tetrafluoride at 120°.[5]

Thiazyl trifluoride, $\mathrm{NSF_3}$, was prepared by the fluorination of $\mathrm{SF_2NCOF}$ with $\mathrm{AgF_2}$.[3] Pentafluorosulfanylamine, $\mathrm{SF_5NH_2}$, was prepared by the reaction of $\mathrm{NSF_3}$ and liquid HF.[2]

Reaction of Pentafluorosulfanylamine with Sulfur Tetrafluoride.—A mixture of 9.1 mmol of $\mathrm{SF_5NH_2}$ and 9.2 mmol of $\mathrm{SF_4}$ was allowed to stand for 40 hr at room temperature. The products were placed over NaF pellets for 2 hr to remove HF and

---

[1] Taken in part from the thesis submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy by Gerald R. Zeilenga.

[2] A. F. Clifford and L. C. Duncan, *Inorg. Chem.*, **5**, 692 (1966).

[3] A. F. Clifford and J. W. Thompson, *ibid.*, **5**, 1424 (1966).

[4] B. Cohen, T. R. Hooper and R. D. Peacock, *Chem. Commun.*, 32 (1966).

[5] A. F. Clifford and C. S. Kobayashi, *Inorg. Chem.*, **4**, 511 (1965).

then passed through −78° (Dry Ice–trichloroethylene), −119° (ethyl bromide slush), and −196° (liquid nitrogen) traps. A small amount of unreacted SF_5NH_2 collected at −78°, while the −196° trap collected SOF_2, which formed from hydrolysis of SF_4. The −119° trap collected a mixture of NSF_3 and $SF_5N{=}SF_2$, which on further fractionation yielded 4.6 mmol of $SF_5N{=}SF_2$, or a 50.6% yield. Products were identified by their infrared spectra. The reaction is

$$SF_5NH_2 + SF_4 \longrightarrow SF_5N{=}SF_2 + 2HF$$

Reaction of Thiazyl Trifluoride and Sulfur Tetrafluoride in Liquid Hydrogen Fluoride.—A mixture of 6.7 mmol of NSF_3 and 23.5 mmol of SF_4 in 5.4 ml of HF was allowed to stand for 48 hr at room temperature. The products were transferred over NaF pellets and warmed for 0.5 hr to remove HF. The mixture collected at −131° (*n*-pentane slush) consisted of NSF_3 and $SF_5N{=}SF_2$. Several collections of the $SF_5N{=}SF_2$ at −112° (1-bromobutane slush) yielded 5.8 mmol of pure $SF_5N{=}SF_2$. This is an 85% yield based on NSF_3. The more volatile products, which passed through the −112° trap and collected at −196°, consisted of SF_4, SOF_2, and SiF_4.

It was necessary to use a large excess of SF_4; otherwise, no unreacted SF_4 was recovered, and yields of $SF_5N{=}SF_2$ were lower. This is probably due to some water in the HF, which would hydrolyze SF_4.

Reaction of Pentafluorosulfanylamine with Phosphorus Pentafluoride.—A 1.77-mmol sample of SF_5NH_2 and 4.21 mmol of PF_5 were allowed to stand for 1 hr at 0° and 1 hr at 25°. The product collected at −30.6° (bromobenzene slush) was an adduct of SF_5NH_2 and PF_5. The more volatile material consisted of NSF_3, POF_3, and PF_5.

Calculations showed that 20% of the SF_5NH_2 had decomposed to form NSF_3, with the remainder forming the adduct. The ratio of SF_5NH_2 to PF_5 in the adduct was found to be 1.08, indicating a 1:1 adduct.

The adduct was only slightly volatile but could be slowly transferred under vacuum. It reacted slowly on standing with glass, forming SF_5NH_2, POF_3, and SiF_4. After heating a sample of the adduct to 155° for 1 hr, most of the sample was recovered unchanged, although some POF_3, SiF_4, SF_5NH_2, and NSF_3 were observed. In addition, a small amount of material was recovered which was characterized by its mass spectrum and infrared spectrum and shown to be the known compound $HN{=}SOF_2$.[6] This must have been formed by the reaction of the adduct with water. After 24 hr at 240°, the adduct had completely decomposed, and NSF_3, POF_3, PF_5, SiF_4, and a trace of $HN{=}SOF_2$ were observed.

Reaction of Pentafluorosulfanylamine with Boron Trifluoride.—The reaction of SF_5NH_2 and BF_3, like the reaction of SF_5NH_2 and PF_5, led to a 1:1 adduct. A mixture of BF_3 and SF_5NH_2 in a 3:1 mole ratio was allowed to stand for 1 hr at 0° and 2 hr at room temperature. The products were passed through −30.6, −131, and −196° traps. The $SF_5NH_2 \cdot BF_3$ collected at −30.6°, and the $NSF_3 \cdot BF_3$ adduct collected at −131°. The excess BF_3 and some SiF_4 collected at −196°. Not all of the starting material was recovered, probably because of hydrolysis of BF_3. However, the SF_5NH_2 used was sufficient to form 0.490 g of 1:1 adduct, and the observed weight of the adduct was 0.492 g.

Reaction of Pentafluorosulfanyliminosulfur Difluoride with Silver Difluoride.—When $SF_5N{=}SF_2$ was heated to 160° for 9 hr in the presence of a large excess of AgF_2, only 3% of the starting material reacted. Even after 24 hr at 217°, only 27% of the starting $SF_5N{=}SF_2$ had reacted. The only products observed were SF_6 and N_2, and in addition some SOF_4 was formed from the AgO impurity in the AgF_2.

Reaction of Pentafluorosulfanyliminosulfur Difluoride with Fluorine.—Reactions were carried out by adding F_2 to $SF_5N{=}SF_2$ at −196° and then allowing the mixture to warm to room temperature and stand for 1 hr. From 1.0 to 2.5 mmol of $SF_5N{=}SF_2$ was normally used in a reaction. Molar ratios of F_2 to $SF_5N{=}SF_2$ varied from 1.2 to 2.2. Carrying out the reaction at 0°, allowing the reaction mixture to warm slowly, or carrying out the reaction in the presence of NaF powder did not affect the yields. When the reaction was carried out over CsF powder, no $(SF_5N{=})_2SF_2$ was obtained.

The reaction products were separated by passing through −78, −119, and −196° traps. The −196° fraction consisted mainly of SF_6, with some SOF_4 and SF_4. The SOF_4 probably formed from OF_2 present as an impurity in the F_2. Depending on the relative amount of fluorine used, from 30 to 70% of the sulfur in the $SF_5N{=}SF_2$ was recovered as SF_6. The −119° fraction consisted of a mixture including unreacted $SF_5N{=}SF_2$ and at least one oxygen-containing compound. The mixture could not be separated by trap-to-trap distillation, and the products were not identified. The −78° fraction consisted of the new compound $(SF_5N{=})_2SF_2$ and a small amount of SiF_4. By collecting the product several times at −78°, the $(SF_5N{=})_2SF_2$ was obtained pure. Yields varied from 8 to 16% of the theoretical values.

Properties of Bis(pentafluorosulfanylimino)sulfur Difluoride, $(SF_5N{=})_2SF_2$.—The product was a clear, colorless liquid with a melting point of −85° and an extrapolated boiling point of 80°. Some difficulty was encountered in obtaining the molecular weight by vapor density measurements because of the solubility of the material in Kel-F No. 90 stopcock grease. The average value was 340, compared with a theoretical value of 352.2. However, the parent peak at m/e 352 was observed in the mass spectrum of the material. The material was stable at room temperature in dry glass but slowly reacted in the presence of moisture with SiF_4 being formed. The vapor pressure was determined using a high-vacuum system with a conventional mercury manometer. The vapor pressure data [T (°C), P (mm)] are: −63.5, 0.0; −30.6, 1.2; −15.0, 4.6; 0.0, 18.1; 13.0, 28.9; 24.5, 52.1.

The heat of vaporization was calculated to be 9.79 kcal/mol, and the Trouton constant to be 27.8.

Results and Discussion

The room-temperature reaction of SF_5NH_2 and SF_4 or, better, the reaction of NSF_3 and SF_4 in liquid HF provided a means of obtaining $SF_5N{=}SF_2$ in yields as high as 85%, much better than the yields previously reported.[3] The reaction in liquid HF probably proceeds with the initial formation of SF_5NH_2, followed by a reaction with SF_4 to form $SF_5N{=}SF_2$ and HF.

When PF_5 or BF_3 reacted with SF_5NH_2, no HF split out and a 1:1 adduct was formed. These adducts were slightly volatile white solids which were extremely easily hydrolyzed.

The $SF_5N{=}SF_2$ showed resistance to fluorination by AgF_2. Even after 24 hr at 217°, only 27% of the starting $SF_5N{=}SF_2$ had reacted, yielding primarily SF_6 and N_2.

The reaction of $SF_5N{=}SF_2$ and F_2 led to large amounts of SF_6, with some unidentified materials and yields of $(SF_5N{=})_2SF_2$ up to 16%. Although they were not detected, it is possible that compounds such as $(SF_5)_2NF$ were in the unidentified materials. This is similar to the reported reaction of perfluoroalkylimino-sulfur difluorides with fluorine.[7] For example, $CF_3N{=}SF_2$ and F_2 yielded $(CF_3N{=})_2SF_2$, CF_3NFSF_5, CF_3NF_2, and SF_6.

Peaks observed at 1350 and 1280 cm^{-1} may be assigned to the symmetric and asymmetric stretches of S=N in -N=S=N-.[3,8,9] Very strong peaks at 920,

---

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

[7] M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4**, 1444 (1965).

[8] A. F. Clifford and C. S. Kobayashi, *ibid.*, **4**, 511 (1965).

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

863, and 592 cm^{-1} are characteristic of the $-SF_5$ group,[2,10,11] and a band at 702 cm^{-1} is also attributable to $-SF_5$.[2,11] A peak at 795 cm^{-1} probably arises from an S—F stretch in $=SF_2=$. Peaks at 725 and 663 cm^{-1} have not been assigned.

The mass spectrum (Table I) was obtained on a Hitachi Perkin-Elmer RMU-6A spectrometer. The molecule ion peak was present at *m/e* 352 with a peak at *m/e* 354, about 13% as intense as the *m/e* 352 peak. This was consistent with three sulfurs in the molecule. Smaller peaks corresponded to the ions containing ^{33}S and ^{15}N isotopes. The largest peak was that for SF_5^+ with the second largest being the SF_3^+ peak. This differs from SF_5NH_2 and $SF_5N{=}SF_2$ mass spectra in which the SF_3^+ peak was more intense than the SF_5^+ peak.

TABLE I

MASS SPECTRUM OF $(SF_5N{=})_2SF_2$

m/e	Rel intens	Species
46	5.5	NS^+
51	2.3	SF^+
65	2.2	NSF^+
70	8.8	SF_2^+
83	2.1	S_2F^+
84	2.0	NSF_2^+
85	2.1	SiF_3^+
89	27.5	SF_3^+
91	1.6	$S^{34}F_3^+$
102	1.3	$S_2F_2^+$
103	5.5	NSF_3^+
108	1.0	SF_4^+
127	100.0	SF_5^+
128	0.8	$S^{33}F_5^+$
129	5.0	$S^{34}F_5^+$
206	1.1	$S_2F_6N_2^+$
333	8.8	$S_3F_{11}N_2^+$
335	1.1	$S^{34}S_2F_{11}N_2^+$
352	5.5	$S_3F_{12}N_2^+$ (molecule ion)
354	0.74	$S^{34}S_2F_{12}N_2^+$

Acknowledgment.—This work was supported by the National Science Foundation under Grant No. GP-4974.

(10) C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964).

(11) L. H. Cross, G. Cushing, and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF IDAHO, MOSCOW, IDAHO 83843

A Simple Preparation of Oxygen Difluoride in High Yield

BY ALAN H. BORNING AND KENT E. PULLEN[1]

Received January 13, 1969

Oxygen difluoride is commonly prepared by bubbling fluorine through a 1-cm layer of 0.5 *N* NaOH with yields up to 50%.[2] A modification of this technique has been reported to produce OF_2 in a yield of 86.79%.[3] The compound has also been produced by various electrolytic methods.[4,5]

In view of recent successes in using CsF or KF to catalyze the preparation of hypofluorites,[6,7] it was thought that OF_2 could be prepared by allowing H_2O to react with F_2 in the presence of an alkali fluoride. This was found to be the case. When F_2 was admitted to a glass bulb containing H_2O and excess CsF, KF, or NaF, a reaction occurred producing OF_2 in yields that ranged from 55 to 80%. Yields were usually above 70% when CsF or KF was used but were generally lower (about 60%) when NaF was employed. Similar experiments were performed in which the alkali fluoride was replaced by powdered NaOH or CaF_2, but in neither case was any appreciable amount of OF_2 obtained.

As a laboratory preparation, this method has the advantage of giving a high yield of OF_2 from a simple reaction. Moreover, the yield is not especially sensitive to either reaction time or variations in the molar ratios of the reactants. Reaction times varied from 15 min to 3 hr, fluorine to water molar ratios varied from 2:1 to 4:1, and alkali fluoride to water molar ratios varied from 2:1 to 100:1. The product is obtained in a very pure state, since HF and SiF_4 (formed from attack of HF on glass) are removed by combining with the catalyst. Oxygen, formed as a by-product, and unreacted fluorine are easily removed by pumping at −196°.

Experimental Section

Standard vacuum-line techniques were employed in all preparations.

When KF was used as a catalyst, H_2O was conveniently added in the form of the commercially available dihydrate, $KF \cdot 2H_2O$. In a typical experiment, 0.327 g (3.48 mmol) of $KF \cdot 2H_2O$, 0.807 g (13.9 mmol) of anhydrous KF, and 0.544 g (14.3 mmol) of F_2 were allowed to react for 1.5 hr in a 500-ml glass bulb. A yield of 5.18 mmol (74%) of OF_2 was obtained. The identity and purity of the product were established from the characteristic infrared and ^{19}F nmr spectra and from the molecular weight (calcd, 54.0; found, 53.4). When CsF or NaF was used as a catalyst, water was added by condensing the desired quantity onto the surface of the anhydrous, powdered catalyst. Since the alkali fluoride tended to cake as the reaction progressed, a few stainless steel balls were added to the glass bulb. Occasional agitation of the balls kept the catalyst powdered. While pumping away O_2 and F_2 from OF_2 at −196°, the pumping time was kept as short as possible in order to minimize loss of product, since OF_2 has an appreciable vapor pressure (~1 mm) at −196°.

Acknowledgments.—The authors are grateful to Professor George H. Cady of the University of Washington for helpful suggestions in connection with this work. A. H. B. was a participant in the National Science Foundation Undergraduate Research Program, Grant No. GY4235.

(1) Author to whom correspondence should be addressed: M. S. 85-85, Organization 2-7817, Aerospace Group, The Boeing Co., Kent, Wash. 98031.

(2) D. M. Yost, *Inorg. Syn.*, **1**, 109 (1939).

(3) R. A. Brown and J. J. Ligi, U. S. Patent 3,367,744 (1968); *Chem. Abstr.*, **68**, 70763 (1968).

(4) A. Engelbrecht and E. Nachbauer, *Monatsh. Chem.*, **90**, 367 (1959).

(5) J. A. Donohue and W. A. Wilson, U. S. Patent 3,276,981 (1966); *Chem. Abstr.*, **66**, 25495 (1967).

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

(7) M. Lustig, A. R. Pitochelli, and J. K. Ruff, *J. Am. Chem. Soc.*, **89**, 2841 (1967).