will be interesting to observe how well the chemistry of the N–H and P–H bonds in difluoramine and difluorophosphine parallel one another.

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Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Pentafluorosulfur and Trifluoromethyl Oxydifluoramines. Preparations and Properties[1]

By WILLIAM H. HALE, Jr., and STANLEY M. WILLIAMSON

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Tetrafluorohydrazine reacts with pentafluorosulfur hypofluorite and trifluoromethyl hypofluorite to form SOF_4, SF_6, FNO, NF_3, and SF_5ONF_2 and COF_2, CF_4, FNO, NF_3, and CF_3ONF_2, respectively. The new difluoramines are colorless, do not react with glass or mercury at room temperature, and have normal boiling points of −10.0 and −60°, respectively, for the pentafluorosulfur and trifluoromethyl oxydifluoramines. The molecular compositions have been proved by physical methods and the reaction schemes for the formation and thermal decomposition of the compounds are given.

Tetrafluorohydrazine is known to exist in equilibrium with NF_2 radicals at room temperature.[2] Many studies, with and without ultraviolet light, have shown that N_2F_4 is an efficient reagent for the introduction of the NF_2 group into organic and inorganic substrates.[3-11]

Since SF_5OF[12] and CF_3OF[13] have been reported to give small amounts of F_5SO and F_3CO radicals upon irradiation with ultraviolet light, it was thought that N_2F_4 should react with SF_5OF and CF_3OF to give SF_5ONF_2 and CF_3ONF_2, respectively. The experiments described below confirm their discovery and characterization.

Experimental

Materials.—Pentafluorosulfur hypofluorite and trifluoromethyl hypofluorite were prepared by the methods of Dudley[14] and Kellogg,[15] respectively. The crude SF_5OF was purified by fractional codistillation[16] and pure SF_5OF was identified by its molecular weight and infrared spectrum. The crude CF_3OF was placed over water for 3 days to remove the COF_2. The gaseous mixture was then led through a trap at −95° and into a trap at −183° where a white solid was collected. The infrared spectrum of this material was identical with the literature spectrum of CF_3OF,[17] although it is possible that some CO_2 was present. A previous report states that CF_3OF is a liquid at −183°.[15] Tetrafluorohydrazine from E. I. du Pont de Nemours and Co. was sufficiently pure to use without additional purification.

Reaction of SF_5OF with N_2F_4.—The gases for this and all other reactions were handled in a vacuum line system with its stopcocks lubricated by No. 90 Kel-F grease. The appropriate quantities of the two reactant gases were condensed in zones in the cold finger of a 1-l. Pyrex glass vessel and then were allowed to warm to room temperature.

The reaction products were separated by means of fractional codistillation[16] and were identified by their molecular weights and characteristic infrared spectra.

Reaction 1.—Pyrex glass vessel at room temperature with initial pressures of 80 mm. for each reactant. The vessel was allowed to stand 17 hr., 8 of which were in the dark. Products found were NF_3, NO, SiF_4, SF_6, SO_2F_2, SOF_4, SF_5ONF_2, and NO_2. The yield of SF_5ONF_2 was 40 mole % with respect to the reactant, SF_5OF, and all of the SF_5OF and N_2F_4 was consumed.

Reaction 2.—Pyrex glass vessel at room temperature with initial pressures of 41 mm. for each reactant. The vessel was allowed to stand for 23 hr., 12 of which were in the dark. All the SF_5OF and N_2F_4 was consumed, but no SF_5ONF_2 was produced. Products observed were NF_3, NO, SiF_4, SF_6, SO_2F_2, SOF_4, and NO_2.

Reaction 3.—The vessel used was a prefluorinated 0.25-in. o.d. closed-end nickel tube fitted with a No. 327 Hoke valve (Teflon seal on stem). The initial pressure of each reactant in the vessel was 4 atm. After 24 hr. at room temperature, no SF_5ONF_2 was observed; 80% of each reactant was recovered unreacted. The remainder of the gas did not contain NO_2 until the gas had contacted the glass vacuum system. This behavior is indicative of the production of FNO as a primary reaction product. Gases present other than SF_5OF, N_2F_4, and NO_2 were NF_3, SiF_4, SF_6, SO_2F_2, and SOF_4.

Reaction 4.—Pyrex glass vessel at room temperature with initial pressures of 140 mm. for each reactant. Ultraviolet irradiation for 21 hr. by a General Electric Type H100-A4/T lamp produced a 60 mole % yield of SF_5ONF_2 (based on the reactant,

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(1) (a) This report is taken from the Ph.D. thesis of W. H. Hale and was presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965. (b) After this paper had been submitted for publication, the authors learned that G. H. Cady and L. C. Duncan had prepared CF_3ONF_2 several years ago, but because of governmental classification they did not report it or continue its characterization.

(2) (a) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **82**, 2400 (1960); (b) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

(3) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(4) J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

(5) R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

(6) C. B. Colburn and F. A. Johnson, *Inorg. Chem.*, **1**, 715 (1962).

(7) G. H. Cady, D. F. Eggers, and B. Tittle, *Proc. Chem. Soc.*, 65 (1963).

(8) M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

(9) E. C. Stump, Jr., C. D. Padgett, and W. S. Brey, Jr., *ibid.*, **2**, 648 (1963).

(10) M. Lustig, C. L. Bumgardner, and J. K. Ruff, *ibid.*, **3**, 917 (1964).

(11) L. C. Duncan and G. H. Cady, *ibid.*, **3**, 1045 (1964).

(12) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 298 (1961).

(13) J. A. C. Allison and G. H. Cady, *ibid.*, **81**, 1089 (1959).

(14) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *ibid.*, **78**, 1553 (1956).

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

(16) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

(17) R. J. Lagemann, E. A. Jones, and P. J. H. Woltz, *J. Chem. Phys.*, **20**, 1768 (1952).

SF_5OF). Some unreacted N_2F_4 and SF_5OF were present and minor amounts of NO, SiF_4, SF_6, SO_2F_2, and NO_2 were formed.

Reaction of CF_3OF with N_2F_4.—Pyrex glass vessel at room temperature with initial pressures of 300 mm. for each reactant. Ultraviolet irradiation for 24 hr. produced a 40 mole % yield of CF_3ONF_2 (based on the reactant, CF_3OF). Other products observed were NF_3, CF_4, and COF_2. A white scaly solid which slowly evolved NO, NO_2, and SiF_4 remained in the flask. About 20% of each reactant was recovered unreacted.

Thermal Decomposition of the Difluoramines.—A 200-ml. Pyrex glass vessel containing 56.5 mm. pressure of SF_5ONF_2 was immersed in a water bath at 85° and within 1 hr. a brown gas appeared. After the flask had been at 85° for 14 hr., analysis of the gas mixture showed that all the reactant had decomposed to give SF_6, NO, NO_2, and SiF_4 in molar ratios of $4.0 \pm 0.2:2.5 \pm 0.2:1.9 \pm 0.2:1$, respectively. Under similar conditions at 190° for 16 hr., CF_3ONF_2 decomposed to give CF_4, NO, NO_2, and SiF_4 in molar ratios of $4.1 \pm 0.2:2.0 \pm 0.2:2.1 \pm 0.2:1$, respectively. Although SF_5ONF_2 decomposed slowly at 75°, decomposition of CF_3ONF_2 did not set in until about 140°. A small amount of a white solid that was decomposed by water remained in the flask in each case.

Properties of SF_5ONF_2 and CF_3ONF_2

Molecular Weights.—From vapor density measurements assuming perfect gas behavior, the average weight per molar volume of SF_5ONF_2 and CF_3ONF_2 was 195.9 and 137.8, respectively. The theoretical values are 195.1 and 137.0, respectively. Neither compound reacted with glass, mercury, Kel-F grease, or sodium chloride.

Melting Points.—Both compounds are white solids at −183° and melt to colorless liquids. A melting point of $-139 \pm 1°$ was obtained for SF_5ONF_2 by visual observation of a sample under autogenous pressure as it warmed in an isopentane cold bath. The melting point of CF_3ONF_2 was not determined. It was a liquid at −160°.

Vapor Pressures and Boiling Points.—For SF_5ONF_2, equilibrium boiling points at a series of fixed pressures were obtained using an apparatus similar to that of Kellogg and Cady.[15] Some representative data are (T, °K., P, mm.): 210.2, 48.5; 219.7, 89.0; 225.4, 123.8; 232.9, 184.5; 238.4, 247.7; 242.8, 312.0; 246.0, 357.7; 250.4, 439.2; 255.8, 558.2; 261.2, 713.6; 264.2, 794.1; 264.9, 822.4. These data can be represented by the equation

$$\log P \text{ (mm.)} = 7.6009 - \frac{1.242 \times 10^3}{T}$$

The maximum deviation of experimentally observed vapor pressures from calculated values is 2.2% (average deviation 0.9%) in the range 48 to 822 mm. pressure. The normal boiling point of SF_5ONF_2 as calculated from this equation is −10.0°. Using the Clausius–Clapeyron equation and assuming ideal gas behavior, the molar heat of vaporization is 5700 cal., corresponding to a Trouton constant of 21.6 cal. mole^{-1} deg.$^{-1}$.

Because of the high volatility of CF_3ONF_2, its vapor pressure curve was determined only approximately by measuring equilibrium vapor pressures at various temperatures as shown by the following data (T, °K., P, mm.): 139.7, 2.3; 162.5, 20.2; 176.5, 77.4; 194.7, 252.0. These data give a normal boiling point of $-60 \pm 1°$.

Mass Spectra.—The mass spectra were obtained from a Consolidated Electrodynamics Corp. Model 103-C mass spectrometer with an ionization potential of 70 volts. As is generally the case in highly fluorinated molecules, the parent ion was not observed for either compound.

The mass spectrum of SF_5ONF_2 beginning at 19 mass units consists of the following (M/Q, species, relative intensity): 19, F^+, 6.3; 30, NO^+, 100.0; 33, NF^+, 0.7; 48, SO^+, 3.4; 49, FNO^+, 1.2; 51, SF^+, 3.8; 52, NF_2^+, 3.3; 67, FSO^+, 12.4; 68, F_2NO^+, 0.2; 70, SF_2^+, 4.2; 86, F_2SO^+, 7.9; 89, SF_3^+, 11.4; 105, F_3SO^+, 8.4; 108, SF_4^+, 2.6; 127, SF_5^+, 28.6. Peaks that corresponded to fragments from SF_5ONF_2 containing S^{33} and S^{34} were observed in the proper abundances along with the corresponding S^{32} peaks.

The mass spectrum of CF_3ONF_2 beginning at 19 mass units consists of the following (M/Q, species, relative intensity: 19, F^+, 2.0; 23.5, FCO^{2+}, 0.4; 28, CO^+, 23.5; 30, NO^+, 61.3; 31, CF^+, 5.4; 33, NF^+, 5.1; 47, FCO^+, 33.8; 49, FNO^+, 0.9; 50, CF_2^+, 0.8; 52, NF_2^+, 85.8; 66, F_2CO^+, 16.0; 69, F_3C^+, 100.0; 85, F_3CO^+, 14.8; 118, F_3CONF^+, 0.1.

Although intense peaks for F_3CO^+ and F_2CO^+ are observed in CF_3ONF_2, the corresponding F_5SO^+ and F_4SO^+ ions are not formed. This is not unexpected since neither F_5SOOSF_5[12] nor F_5SOCF_3[18] forms the F_5SO^+ or F_4SO^+ ions.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were obtained using a Varian Associates HR-60 n.m.r. spectrometer with a 56.4-Mc. radiofrequency probe for use in F^{19} resonance work. A reproduction of the spectrum of SF_5ONF_2 is given in Figure 1, in which the NF_2 and SF_5 resonances are shown on different ordinate and abscissa scales. The zero value in Figure 1 corresponds to the center of the SF_4 resonance. The sulfur–fluorine nuclear resonance is typical of the SF_5 group in that there is considerable second-order spin–spin interaction between the apical and the four basal fluorine atoms. Preliminary determination of line positions and chemical shift between the two types of sulfur fluorine atoms was done using the method of Merrill, Williamson, Cady, and Eggers.[19] The chemical shift obtained in this manner was used in combination with J_{AB} values of 150.0, 152.0, and 154.0 c.p.s. as suggested by Merrill, *et al.*,[19] for calculations of the AB_4 spectrum on an I.B.M. 7094 computer using the method of McConnell, McLean, and Reilly.[20] Excellent agreement between the experimental and calculated spectra was obtained for the selected value of J_{AB} = 154.0 c.p.s. and the experimentally determined δ = 4.45 p.p.m. The apical fluorine nuclear resonance is upfield from that of the basal fluorines as is usually the

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[18] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 850 (1964).

[19] C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *ibid.*, **1**, 215 (1962).

[20] H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

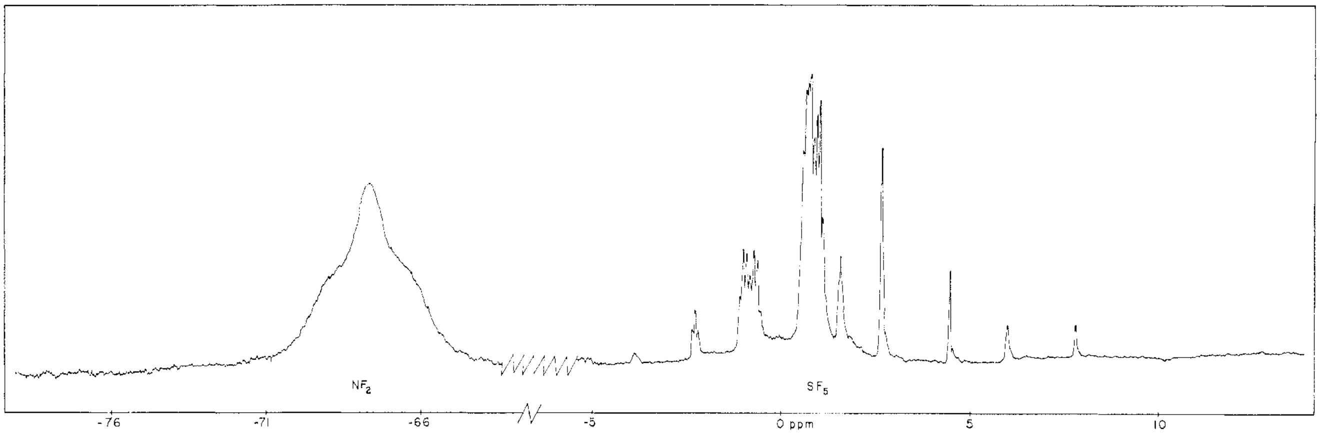

Figure 1.—N.m.r. spectrum of SF_5ONF_2.

case for SF_5O groups.[19] Peak areas of the three different types of fluorine atoms were close to the ratio of 1:4:2 as would be expected for FSF_4ONF_2. Experimental peak areas were $1:4.2 \pm 0.2:2.1 \pm 0.2$.

The n.m.r. spectrum of CF_3ONF_2 shows two resonances with an upfield to downfield peak area ratio of 1.6 ± 0.2. The upfield resonance, due to the CF_3 fluorines, is split into a sharp 1:2:1 triplet by the NF_2 fluorine atoms. The downfield resonance is a very broad triplet caused by splitting of the NF_2 fluorine atom resonance by the N^{14} quadrupole moment.

A summary of the experimental n.m.r. data for SF_5ONF_2 and CF_3ONF_2 is given in Table I.

Table I

Chemical Shifts and Spin–Spin Coupling Constants for SF_5ONF_2 and CF_3ONF_2

$\overset{1}{F}\overset{2}{S}F_4\text{–O–}\overset{3}{N}F_2$

$\delta_{12} = 4.45$ p.p.m. $J_{12} = 154.0$ c.p.s.
$\delta_{23} = 67.66$ p.p.m. $J_{13} = 0$
$J_{23} = 3.8$ c.p.s.

$\overset{1}{F_3}C\text{–O–}N\overset{2}{F_2}$

$\delta_{12} = 188.9$ p.p.m. $J_{12} = 3.2$ c.p.s.
$J_{N^{14}-\overset{2}{F}} = 125.7$ c.p.s.

Infrared Spectra.—The infrared spectra reproduced in Figures 2 and 3 were obtained on a Perkin-Elmer Model 421 grating spectrophotometer using a Pyrex cell with 9-cm. path length and NaCl windows. Polystyrene calibration indicates that the reported values are accurate within 3 cm.$^{-1}$. The data obtained are summarized in Table II.

Table II

Infrared Data of SF_5ONF_2 and CF_3ONF_2

SF_5ONF_2				CF_3ONF_2			
Cm.$^{-1}$	Rel. int.	Cm.$^{-1}$	Rel. int.	Cm.$^{-1}$	Rel. int.	Cm.$^{-1}$	Rel. int.
1966	vw	1130	vw	2598	vw	1296	vs
1908	vw	1091	vw	2525	vw	1243	vs
1843	vw	1029	s	2420	vw	1215	vs
1706	vw	928	vvs	2233	vw	1066	m
1639	w	858	vs	2150	m	1027	s
1620	w	844	vs	1921	vw	933	s
1575	w	786	vs	1797	vw	892	s
1304	vw	706	s	1745	vw	865	vs
1226	w	~600	vs	1560	vw	712	s
1154	vw			1494	vw	628	m
				1411	vw		

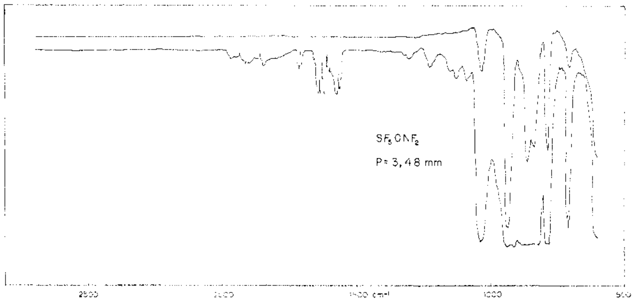

Figure 2.—Infrared spectrum of SF_5ONF_2.

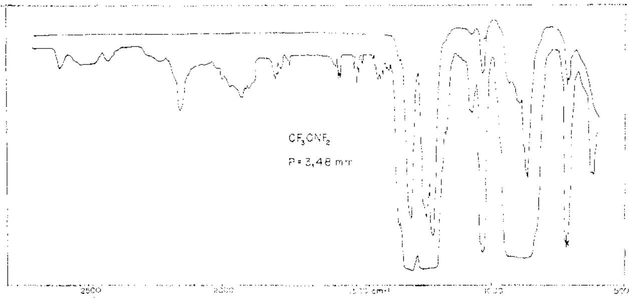

Figure 3.—Infrared spectrum of CF_3ONF_2.

The assignments for the intense bands along with the data on which these assignments are based are given in Table III.

The frequencies of the asymmetric in-plane SF_4-square stretch and the asymmetric N–F stretch lie very close together. For SF_5ONF_2, we feel that these two bands overlap and could explain the unusual intensity of the band at 928 cm.$^{-1}$. Also lying close together are the N–O and S–F stretching frequencies. For SF_5ONF_2 both bands are observed (at 858 and 844 cm.$^{-1}$), but their assignment is uncertain. The symmetric out-of-plane SF_4-square deformation around 600 cm.$^{-1}$ was not determined exactly because of the NaCl cutoff at this frequency.

The PQR branching observed in the bands at 712 and 706 cm.$^{-1}$ affords additional evidence for assign-

TABLE III

INFRARED FREQUENCY ASSIGNMENTS FOR CF_3ONF_2 AND SF_5ONF_2 (ν IN CM.$^{-1}$)

Compound	ν_A	ν_B	ν_C	ν_F	ν_G	ν_H	ν_I	ν_J
CF_3ONF_2	1296	1243	1215	1027	933	712	892	865
CF_3OF[a]	1282	1259	1220				880	
CF_3OSF_5[b]	1275	1238	1198					
NF_3[c]				1032	905	647		
SF_5NF_2[d]				1029	946	679		
NF_2OSO_2F[e]				1032	913			
CH_3ONH_2[f]								858

Compound	ν_D	ν_E	ν_F	ν_G	ν_H	ν_J	ν_K	ν_L
SF_5ONF_2	~928	~600	1029	~928	706	858?	844?	786
SF_5OCF_3[b]							854	
NF_3[c]			1032	905	647			
SF_5NF_2[d]	912	605	1029	946	679			
NF_2OSO_2F[e]			1032	913				778
SF_6[g]	940	615						
SF_5Cl[h]	908	599						
SF_5OF[i]	935	637						
FSO_2OF[j]							852	789
SO_2F_2[k]							852	
SF_5OOSF_5[l]							848	
CH_3OSO_2F[j]							857	787

$\nu_A \equiv$ CF_3 asym. str.
$\nu_B \equiv$ CF_3 asym. str.
$\nu_C \equiv$ CF_3 sym. str.
$\nu_D \equiv$ asym. in-plane SF_4-square str.
$\nu_E \equiv$ sym. out-of-plane SF_4-square def.
$\nu_F \equiv$ N–F sym. str.
$\nu_G \equiv$ N–F asym. str.
$\nu_H \equiv$ NF_2X sym. def.
$\nu_I \equiv$ C–O str.
$\nu_J \equiv$ N–O str.
$\nu_K \equiv$ S–F str.
$\nu_L \equiv$ S–O str.

[a] See ref. 17. [b] See ref. 18. [c] M. K. Wilson and S. R. Polo, *J. Chem. Phys.*, **19**, 534 (1951). [d] See ref. 7. [e] See ref. 8. [f] M. Davies and N. A. Spiers, *J. Chem. Soc.*, 3971 (1959). [g] R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, **19**, 534 (1951). [h] L. H. Cross, H. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1960). [i] See ref. 14. [j] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 290 (1956). [k] W. D. Perkins and M. K. Wilson, *J. Chem. Phys.*, **20**, 1791 (1952). [l] See ref. 12.

ment of these bands to the NF_2X symmetric deformation since this would be a parallel vibration of a near symmetric top.

Discussion

In addition to the formation of SF_5ONF_2 and CF_3ONF_2, the respective hypofluorites act both as fluorinating and oxidizing agents to N_2F_4. Fluorination reactions of SF_5OF with CO,[21] SOF_2,[12] and SO_2[22] produce SOF_4 and COF_2, SOF_4, and SO_2F_2, respectively. The corresponding reactions of CF_3OF with SO_2,[23] sulfur,[24] and various organic compounds[13] produce COF_2 and SO_2F_2, SF_4, and fluorinated hydrocarbons, respectively.

The fluorination reactions that are occurring in our work are

$$SF_5OF + N_2F_4 \longrightarrow SOF_4 + 2NF_3 \tag{1}$$

$$CF_3OF + N_2F_4 \longrightarrow COF_2 + 2NF_3 \tag{2}$$

Pentafluorosulfur hypofluorite can oxidize SO_2 to SO_3[22] and CCl_4 to COF_2,[21] whereas CF_3OF oxidizes SO_2 to a mixture of several compounds such as CF_3OSO_2F, $(CF_3)_2SO_4$, etc.[23]

Beach[25] has reported the oxidation of N_2F_4 by air.

$$N_2F_4 + {}^1/_2O_2 \longrightarrow FNO + NF_3 \tag{3}$$

In a moist glass system, Beach noticed SiF_4 and NO_2 and no FNO. The products from our reactions suggest that the hypofluorites oxidize N_2F_4 in the following manner.

$$SF_5OF + N_2F_4 \longrightarrow FNO + NF_3 + SF_6 \tag{4}$$

$$CF_3OF + N_2F_4 \longrightarrow FNO + NF_3 + CF_4 \tag{5}$$

Reactions 4 and 5 are analogous to reaction 3. Ruff, Menzel, and Neumann[26] have studied the reaction of FNO and glass.

$$4FNO + SiO_2 \longrightarrow SiF_4 + 2NO + 2NO_2 \tag{6}$$

Therefore, all of the by-products found in our reactions are accounted for by the appropriate reactions above, except for the traces of SO_2F_2 which most likely are produced by some decomposition of the SOF_4 or transient F_5SOOSF_5.[12]

$$2SOF_4 \longrightarrow SO_2F_2 + SF_6 \tag{7}$$

In these reactions, FNO is absorbed by SiO_2 to form a white, scaly compound which slowly evolves NO, NO_2, and SiF_4 *in vacuo*. Evolution of these gases occurs in all-glass systems as well as systems in contact with Kel-F stopcock grease. It is felt that the NO_2 observed must come from FNO + glass, because when SF_5OF and N_2F_4 are allowed to react in a nickel vessel, no brown gas was present until the product gases had been exposed to the glass vacuum system for a minute or so.

As an additional check on the role of FNO in the reaction, SF_5OF and NO gave only SOF_4, SiF_4, NO, and NO_2 in a Pyrex glass reaction vessel, but from a nickel vessel, rapid infrared analysis of the product gases showed FNO and SOF_4 to be present, probably from the following fluorination reaction.

$$SF_5OF + 2NO \longrightarrow SOF_4 + 2FNO \tag{8}$$

For maximum yield of the addition compounds, N_2F_4–hypofluorite reactions should be run at high pressures in the presence of ultraviolet light. The extreme pressure dependence of the N_2F_4–SF_5OF reaction is shown by the 40% yield of SF_5ONF_2 starting with 80 mm. of each of the reactants and the total lack of SF_5ONF_2 formation starting with 41 mm. of each reactant. However, light is necessary since reactions in the dark with 4 atm. each of N_2F_4 and SF_5OF produced no SF_5ONF_2.

The relatively low rates of the photolytic addition reactions could probably be increased by using quartz apparatus since Pyrex glass is a poor transmitter of the higher-energy mercury lamp radiation. The relative yields of the addition compounds might be increased since the side reactions are probably not photolytic.

The thermal decomposition products and relative amounts are consistent with the reactions

$$F_5SONF_2 \xrightarrow{\Delta} F_5S\cdot + \cdot ONF_2 \longrightarrow SF_6 + FNO \tag{9}$$

$$F_3CONF_2 \xrightarrow{\Delta} F_3C\cdot + \cdot ONF_2 \longrightarrow CF_4 + FNO \tag{10}$$

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(21) S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

(22) G. Pass and H. L. Roberts, *ibid.*, **2**, 1016 (1963).

(23) W. P. van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960).

(24) R. L. Porter and G. H. Cady, *ibid.*, **79**, 5625 (1957).

(25) L. K. Beach, *J. Inorg. Nucl. Chem.*, **26**, 2033 (1964).

(26) O. Ruff, W. Menzel, and W. Neumann, *Z. anorg. allgem. Chem.*, **208**, 293 (1932).

followed by eq. 6. Approximate calculations of ΔH show that eq. 9 and 10 are the favored reactions despite the weakness of the O–N bond ($\sim$35 kcal.)[27] relative to the S–O ($\sim$65 kcal.)[27] and C–O ($\sim$81 kcal.) bonds. Rupture of the O–N bond would lead to SOF_4 (or COF_2) and NF_3. None of the latter compounds was obtained. A higher temperature is required for the decomposition of CF_3ONF_2 than for SF_5ONF_2 because of the greater strength of the C–O bond relative to the S–O bond.

Acknowledgments.—We wish to thank Mr. James A. Ferretti for his assistance with the calculated and experimental n.m.r. spectra. W. H. H. appreciates the financial assistance given by the Standard Oil Company of California.

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[27] G. S. Paulett and M. Lustig, *J. Am. Chem. Soc.*, **87**, 1020 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Molecular Structure and Bonding of $N_2(CF_3)_4$. An Electron Diffraction Study[1,2]

BY L. S. BARTELL AND H. K. HIGGINBOTHAM

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The molecule $(CF_3)_2NN(CF_3)_2$ represents an interesting example in which, paradoxically, a bond appears to be strengthened and shortened by virtue of strong nonbonded repulsions across it. The substance has been reported to be exceptionally stable to thermal decomposition, and its central N–N bond was observed in this study to be perhaps 0.05 Å. shorter than its counterpart in N_2H_4. The crowding of trifluoromethyl groups is found to flatten the two >N– pyramids almost to planarity and to set the dihedral angle between opposite $-N(CF_3)_2$ groups at a value of about 90°. A molecular orbital description suggests that the short N–N bond may be understood in terms of the enhancement of π bonding ensuing from the nearly D_{2d} symmetry imposed by steric forces. Structural parameters and amplitudes of vibration of the free (gaseous) molecules were determined by electron diffraction. All bond lengths except for N–N were found to be normal. The large deformations from normal bond angles lead to a rather efficient solution of the molecule's steric problems. Nonbonded repulsions are not borne by a few highly compressed atoms but are distributed among two dozen atom pairs in normal van der Waals contact.

Introduction

The compound tetrakis(trifluoromethyl)hydrazine poses several interesting questions. It has been reported by Young and Dresdner[3] to be enormously more stable to the thermal rupture of its N–N bond than a number of other hydrazine derivatives. Its stability is even more remarkable when it is considered that it is among the most crowded of the derivatives studied and must suffer substantial repulsions between its bulky CF_3 groups. If the molecule were assumed to have normal bond lengths and to have bond angles similar to those of hydrazine itself, the implied nonbonded F···F distances would be almost 1 Å. shorter than any nongeminal F···F distances ever observed. Since such short distances are highly improbable it seemed worthwhile to investigate the deformations in structure introduced by steric stress. It was hoped that a structural analysis might also shed light on the surprising stability of the substance.

Experimental

A sample of $N_2(CF_3)_4$ was donated by Professor John A. Young. Gas phase chromatography indicated that the compound was approximately 99% pure. Diffraction patterns were taken with the Iowa State University sector electron diffraction apparatus[4] using a sample pressure of 15 torr. Absorbancies of diffraction patterns were converted to intensities in a manner described elsewhere.[4-6]

Structure Analysis

Leveled experimental intensities $I_0(q)$ were converted to reduced molecular intensities by the procedure outlined in ref. 6. The leveled intensities and associated background functions are shown in Figure 1. Experimental radial distribution functions, incorporating a modification function $\exp(-0.00166s^2)$, were calculated using theoretical data for the range $q = 0$ to $q = 16$ and experimental data for $q = 17$ to $q = 120$.

The experimental distribution curves bore scant resemblance to a variety of initial synthetic curves calculated for plausible molecular parameters. Therefore it was decided to make some rather severe simplifying assumptions about the structure and to optimize parameters before relaxing the assumptions.

It is reasonable to expect the present molecule to have C_2 symmetry and, accordingly, 25 independent structural parameters. If all C–F bonds are assumed to have the same length, all C–N bond lengths are taken

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[2] Based in part on a dissertation by H. K. Higginbotham to the Graduate School, Iowa State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

[3] J. A. Young and R. D. Dresdner, *J. Org. Chem.*, **28**, 833 (1963).

[4] L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.*, **35**, 1211 (1961).

[5] L. S. Bartell and L. O. Brockway, *J. Appl. Phys.*, **24**, 656 (1953).

[6] R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).