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Technical Report No. 45

to the

Office of Naval Research

ARPA Order No. 26-60, Task 2, Item 3

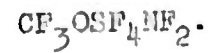
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THE PREPARATION OF  
DIFLUOROAMINOTRIFLUOROMETHOXYTETRAFLUOROSULFUR (VI),

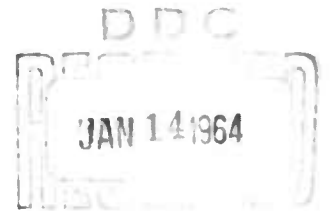


by

Leonard C. Duncan and George H. Cady

Department of Chemistry  
University of Washington  
Seattle 5, Washington

1963



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THE PREPARATION OF DIPLUOROAMINOTRIFLUOROMETHOXY-  
TETRAFLUOROSULFUR(VI),  $CF_3OSF_4NF_2$

by

Leonard C. Duncan and George H. Cady

Trifluoromethyl hypofluorite reacts with sulfur tetra-  
fluoride to form  $CF_3OSF_5$ <sup>(1,2)</sup> and  $(CF_3O)_2SF_4$ <sup>(2)</sup>. If oxygen<sup>(1)</sup>

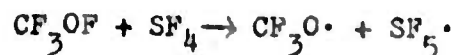
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(1) G. Pass and H. L. Roberts, J. Inorg. Chem., 2, 1016 (1963).

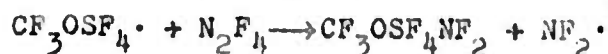
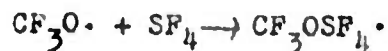
(2) Leonard C. Duncan and George H. Cady, in print.

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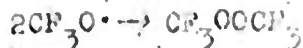
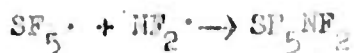
is present the compounds  $CF_3OSF_4OSF_5$ ,  $CF_3OSF_4OOSF_5$ , and  $CF_3OSF_4OOSF_4OCF_3$   
are also formed. In this investigation,  $CF_3CF$  and  $SF_4^+$  were  
allowed to react in the presence of  $N_2F_4$  in order to learn whether  
a product containing both  $NF_2$  and  $CF_3O$  groups would be formed.  
This turned out to be the case. The reaction may have proceeded  
by a series of steps such as proposed by G. Pass and H. L. Roberts<sup>(1)</sup>  
with an initiation step such as



and then further steps as



and termination as



The  $\text{NF}_2$  and  $\text{CF}_3\text{O}$  groups were found to be located in *cis* positions with respect to each other.

#### EXPERIMENTAL

Reactions.--In a typical reaction 3.3 g. of  $\text{N}_2\text{F}_4$ , 1.3 g. of  $\text{SF}_4$ , and 3.8 g. of  $\text{CF}_3\text{CF}_3$  were held in a 10 cc. Monel reactor at room temperature for seven days. The tube was then opened and the volatile products were separated by fractional codistillation.<sup>(3)</sup> They were, in order of decreasing volatility,

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(3) G. H. Cady and D. P. Stegwarth, *Anal. Chem.*, **31**, 613 (1959).

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$\text{CF}_3\text{OF}$ ,  $\text{SiF}_4$ ,  $\text{COF}_2$ ,  $\text{N}_2\text{F}_4$ ,  $\text{F}_2$ ,  $\text{SOF}_2$ ,  $\text{CF}_3\text{OOCF}_3$ ,  $\text{SF}_5\text{NF}_2$ , and  $\text{CF}_3\text{OSF}_4\text{NF}_2$  (~14%). All the above substances except the unidentified material and the least volatile product were identified by their characteristic infrared spectra.

Properties of d-fluoroaminotrifluoromethoxytetrafluoro-sulfur(VI).--Experimental measurements gave an average molecular weight of 245.1 compared to a molecular weight of 245.1 calculated for  $\text{CF}_3\text{OSF}_4\text{NF}_2$ . Densities at five temperatures shown in Table 1 correspond to a volume coefficient of expansion at 0° of  $2.07 \times 10^{-3}$ .

Table I

Densities of  $\text{CF}_3\text{OSF}_4\text{NF}_2$ 

Temp. °	0.0	8.8	15.3	27.9	33.3
Density g/cc	1.827	1.793	1.770	1.726	1.702

Vapor pressures shown in Table 2 indicate a heat of vaporization from the Clausius-Clapeyron equation of 6.87 kcal/mole, a normal boiling point of 29.3°, and a Trouton constant of 22.7 eu. The experimental data fit the expression  $\log_{10} P_{\text{mm}} = \frac{-1.5011}{T} \times 10^5 + 7.3767$ .

Table II

Vapor Pressures of  $\text{CF}_3\text{OSF}_4\text{NF}_2$ 

$P_{\text{mm}}$	Temp °K.	$P_{\text{mm}}$	Temp °K.
109.0	257.1	459.0	288.2
127.2	260.0	490.6	289.4
145.9	262.7	527.8	291.2
204.4	269.4	567.1	293.2
233.1	273.0	596.9	294.2
270.0	275.4	628.5	295.2
297.9	277.5	662.5	297.2
324.5	279.7	698.2	298.2
360.7	282.4	(760.0)	(302.5)
390.6	285.2		
425.4	286.3		

The infrared spectrum of  $\text{CF}_3\text{OSF}_4\text{NF}_2$  is shown in Table III.

Table III

Infrared Spectrum of  $\text{CF}_3\text{OSF}_4\text{NF}_2$ 

Frequency, $\text{cm.}^{-1}$	Assignment	Frequency, $\text{cm.}^{-1}$	Assignment
1271 vs	CF str <sup>(4)</sup>	942 s	
1245 vs	CF str	902 s	
1187 vs	CF str	855 s	
1124 s	NF str <sup>(5)</sup>	830 vs	
981 s		755 m	
		709 m	SF str <sup>(6)</sup>

(4) J. H. Simons, Fluorine Chemistry, Academic Press, Inc., New York, Vol. II, 1950, p. 456.

(5)  $\text{NF}_3$  has NF Stretch in this Region, H. H. Wilson and S. R. Polo, J. Chem. Phys. 20, 1716 (1952).

(6)  $\text{SF}_5\text{Cl}$  and  $\text{SF}_5\text{Br}$  have medium absorption in this region.

The compound is colorless and slowly reacts with glass at room temperature forming  $(\text{NO})_2\text{S}_2\text{F}_6$ . The analysis for nitrogen was carried out by weighing the volatiles after the reaction of this material with molten potassium. Found: nitrogen 5.8%. Theoretical: nitrogen 5.72%. The analysis for fluorine was carried out by comparing the integrated  $\text{F}^{19}$  CF n.m.r. resonance areas of samples containing known weights of  $\text{CF}_3\text{OSF}_4\text{NF}_2$  and  $\text{CCl}_3\text{F}$ . Found: 23.43% CF fluorine. Theoretical: 23.25% CF fluorine. The integrated  $\text{F}^{19}$  n.m.r. resonance areas of a pure sample of the compound indicated that for every 3 fluorine atoms bound to carbon, there were 2.01 bound to nitrogen, and 4.03

bound to sulfur. The total fluorine found: 71.1%. Theoretical: 69.8%. The  $F^{19}$  n.m.r. spectrum of  $CF_3OSF_4NF_2$  at 56.4 Mc is shown in Fig. 2. The SF portion of the spectrum corresponded to the *cis*-structure  $\Delta_1$  which the  $F^{19}$  n.m.r. spectrum was that of an  $A_2BCX_3Y_2$  system having the two Y atoms attached to nitrogen. The spin couplings  $J_{NF-SF_{A_2}}$ ,  $J_{NF-SF_B}$ ,  $J_{NF-SF_C}$ ,  $J_{CF-SF_{A_2}}$ ,  $J_{CF-SF_B}$  and  $J_{CF-SF_C}$  were estimated from both 40 and 56.4 Mc spectra (see table V). These coupling values were then used to estimate the position of the S-F resonance lines, and a theoretical spectrum was calculated for an  $A_2EC$  model. It was found that the computed spectrum was in fair agreement with the  $SF_4$  portion of the experimental spectrum when the spin coupling constants and chemical shifts shown in Table V were used. The "spike" at lower field than the  $NF_2$  resonance was not identified.

Table V  
 $F^{19}$  Spin Coupling Constants and Chemical Shifts  
 for  $CF_3OSF_4NF_2$  NMR Spectrum

"Types" fluorine atoms	J, cps	ppm, difference for the two "types" of F atoms	ppm, compared to the $CF_3$ group $\frac{H-Hr}{Hr} \times 10^6$
B - A	160.0	2.60	
B - C	149.2	23.27	
A - C	140.0	20.66	
X - B	1.0		-100.4
X - A	12.8		-103.0
X - C	12.8		-123.7
X - Y	?		-131.8
X - impurity "spike"	0		-136.0
Y - B	22.3		
Y - A	21.8		
Y - C	2.4		
Nitrogen - Y	110		

The proximity of the calculated and experimental spectra indicates that the proposed structure is correct. A comparison of the CF - SF and NF - SF coupling constants with those of related compounds supports a structure with a F<sub>3</sub>CO and an NF<sub>2</sub> group attached to the sulfur atom of the SF<sub>4</sub> group.

Table VI

<sup>19</sup>F Coupling Constants of S-F Compounds

Compound	"Type" Fluorine Coupling	J, cps
CF <sub>3</sub> SF <sub>5</sub> (7)	CF <sub>3</sub> - SF <sub>A4</sub>	22.4
	SF <sub>2</sub> - SF <sub>B</sub>	6.4
CF <sub>3</sub> OSF <sub>5</sub> (7)	CF <sub>3</sub> - SF <sub>A4</sub>	9.9
	CF <sub>3</sub> - SF <sub>B</sub>	1.5
(cis) (CF <sub>3</sub> O) <sub>2</sub> SF <sub>4</sub> (2)	CF <sub>3</sub> - SF <sub>A2</sub>	9.0
(trans)CF <sub>3</sub> SF <sub>4</sub> NF <sub>2</sub> (8)	CF <sub>3</sub> - SF <sub>A4</sub>	22
	NF <sub>2</sub> - SF <sub>A4</sub>	20
NF <sub>2</sub> SF <sub>5</sub> (9)	NF <sub>2</sub> - SF <sub>A4</sub>	19.1
	NF <sub>2</sub> - SF <sub>B</sub>	4.1
FSO <sub>3</sub> NF <sub>2</sub> (10)	NF <sub>2</sub> - SF	6

(7) C. I. Merrill, S. M. Williamson, G. H. Cady and D. F. Eggers, Jr., J. Inorg. Chem., 1, 215 (1962).

(8) A. L. Logothetis, G. N. Sausen, R. J. Stoda, J. Inorg. Chem., 2, 173 (1963).

(9) These values were obtained from the spectrum of this compound reported by G. H. Cady, D. F. Eggers, Jr., and B. Tittle, Proceedings Chem. Soc., 55-6 Feb. (1963).

(10) M. Lustig and G. H. Cady, J. Inorg. Chem., 2, 388 (1963).

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The respective  $CF_3$ -SF coupling constants in  $CF_3OSF_4NF_2$  are of a magnitude that might be expected for a  $CF_3$  group bound through oxygen, interacting with sulfur fluorines at  $90^\circ$  and  $180^\circ$ . The observed NF-SF coupling constants are also within the range that might be expected for a  $NF_2$  group bound directly to sulfur. The cis structure of the compound is in accord with the reported structures of other derivatives of  $SF_6$  formed by direct oxidation of  $SF_4$ , cis- $(FSO_3)_2SF_4$ ,<sup>(11)</sup> cis- $(F_5SO)_2SF_4$ ,<sup>(12)</sup> and cis- $(CF_3O)_2SF_4$ .<sup>(2)</sup>

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(11) Jean'ne M. Shreeve and G. H. Cady, J. Amer. Chem. Soc., 83, 4521 (1961).

(12) C. I. Merrill and G. H. Cady, J. Amer. Chem. Soc., 85, 909 (1963).

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ACKNOWLEDGEMENTS - This work was performed in part under contract with the Office of Naval Research and in part under a fellowship of the Allied Chemical Co. The n.m.r. spectra were acquired by B. J. Nist.

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