

1:1 ADDUCTS OF SF<sub>4</sub> WITH TETRAHYDROFURAN AND DIETHYLETHER

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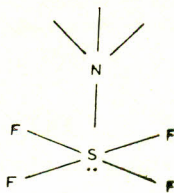
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The F<sup>19</sup> NMR spectra of SF<sub>4</sub>-THF and SF<sub>4</sub>-Et<sub>2</sub>O systems were investigated between room temperature and -70°C in the case of the former and -132°C in the case of the latter. The spectral analysis indicates that SF<sub>4</sub> and the ether interact at low temperatures forming 1:1 adducts. A *trans* structure has been proposed for the adducts.

**Introduction**

Muetterties *et al.*<sup>1</sup> have reported the preparation of adducts between SF<sub>4</sub> and tertiary amines, e.g., pyridine, trimethyl amine and *N*-methylmorpholine, etc. They found that the adducts give a single sharp fluorine resonance peak. Therefore, they concluded that the adduct has the following square pyramidal structure:



They also studied the SF<sub>4</sub>-THF\* system, but did not find any evidence for adduct formation; nevertheless, they did observe that the fluorine exchange was slowed down. Muetterties *et al.*<sup>1</sup> did not report the temperature at which the F<sup>19</sup> NMR spectrum was examined. However, in an investigation involving the solutions of SF<sub>4</sub> in tetrahydrofuran it was observed that the fluoride could not be distilled under high vacuum at about -80° although the melting point of SF<sub>4</sub> is -121°<sup>2</sup> and that of tetrahydrofuran is -108°.<sup>3</sup> The reasons for this observation could be that SF<sub>4</sub>, a weak electrophile, and tetrahydrofuran, a fair donor, form a molecular complex which has a very low vapour pressure at -80°. Diethyl ether is also a weak nucleophile; it was expected that probably it would also form a weak complex with SF<sub>4</sub> at low temperatures. Consequently the fluorine-19 NMR spectra of the SF<sub>4</sub>-THF system and the SF<sub>4</sub>-Et<sub>2</sub>O system were studied at various temperatures.

\* THF, Tetrahydrofuran.

**Experimental**

The Pyrex glass NMR tube was vacuum dried. Purified SF<sub>4</sub> and the dry ether (THF or Et<sub>2</sub>O) were distilled under vacuum into the tube and the tube was sealed under vacuum. The NMR spectra were taken at 56.4 Mc/s and 1400 gauss employing a Varian High Resolution NMR Spectrometer Model 4300 B.

**F<sup>19</sup> NMR SPECTRUM OF SF<sub>4</sub>-THF SYSTEM**

The fluorine-19 resonance spectrum of the freshly prepared sample was taken between room temperature and -80°C. At room temperature two very broad peaks were observed. As the temperature was lowered, the peaks also began to narrow; at -25°C to -30°C they became sharp and showed a triplet structure. At -67°C the appearance of the spectrum remained unchanged, and when the temperature was lowered to -70°, the fluorine signal disappeared. The NMR spectra of SF<sub>4</sub>-THF system at different temperatures are shown in Fig. 1.

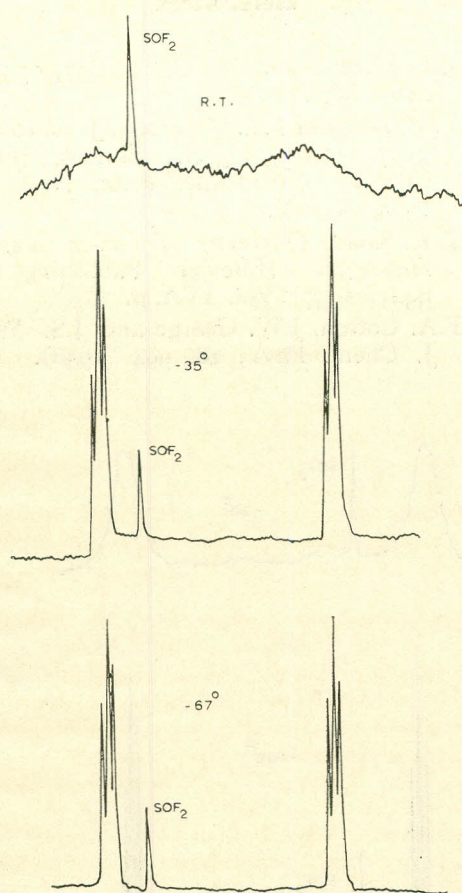
**F<sup>19</sup> NMR SPECTRUM OF SF<sub>4</sub>-ETHER SYSTEM**

The F<sup>19</sup> NMR spectrum of SF<sub>4</sub>-Et<sub>2</sub>O was observed between room temperature and -132°C. At room temperature one very broad peak, about 1600 cycles wide, was observed and found to split into two broad peaks at -5°C. As the temperature was lowered, the two peaks narrowed. At -35°C these peaks showed a triplet structure and were resolved into two well-defined triplets at -45°. The F<sup>19</sup> NMR spectra of SF<sub>4</sub>-Et<sub>2</sub>O at various temperatures are shown in Fig. 2.

The chemical shifts of the two triplets and the coupling constants of the two systems are given in Table 1.

**Discussion**

In the system SF<sub>4</sub>-THF the fluorine resonance signal of SF<sub>4</sub> was resolved into two sharp triplets

Fig. 1.—F<sup>19</sup> NMR spectra of SF<sub>4</sub>—THF.

at -25°C. The chemical shifts at -40°C and -67°C were found to be 47.1 ppm and 45.3 ppm respectively and the coupling constant was found to be 66.4 c/s (Table 1). In the system SF<sub>4</sub>-Et<sub>2</sub>O the F<sup>19</sup> NMR signal of SF<sub>4</sub> was split into two well-defined triplets at -45°C. The chemical shifts at -50°C and -132°C were found to be 51.8 ppm and 48.1 ppm and the coupling constant was found to be 66.4 c/s. Cotton *et al.*<sup>4</sup> and Muettterties *et al.*<sup>5</sup> have reported that the coupling constant of the SF<sub>4</sub> triplets at -100°C is 78 c/s and that the F<sup>19</sup> resonance signal splits into two equal resonances at -47°C which become resolved at -85°C. Muettterties reported the chemical shift between these triplets to be 52 ppm. Later work by Quail<sup>6</sup> has shown that the effect of temperature on the separation of the two triplets is not very significant. The chemical shifts of the two triplets at -59°C and -103°C were found to be 53.2 and 52.0 ppm respectively and the coupling constant was found to be 76.4 c/s (Table 1). On the basis of these observations it is suggested that SF<sub>4</sub> and the ether, *viz.*, THF or Et<sub>2</sub>O, form a (1:1) molecular complex which is stable at low temperature. Since the fluorine resonance spectra of the adducts are composed of two triplets, the following structure is proposed.

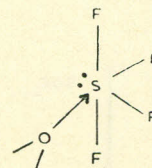


TABLE I.—CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SF<sub>4</sub>, SF<sub>4</sub>-Et<sub>2</sub>O AND SF<sub>4</sub>-THF TRIPLETS.

Temperature	Chemical shifts between the two F <sup>19</sup> resonances in ppm			Coupling Constant J <sub>FF</sub> in c/s		
	SF <sub>4</sub> (6)	SF <sub>4</sub> -THF	SF <sub>4</sub> -Et <sub>2</sub> O	SF <sub>4</sub>	SF <sub>4</sub> -THF	SF <sub>4</sub> -Et <sub>2</sub> O
-25°	—	—	52.4	—	—	—
-28°	53.9	—	—	—	—	—
-35°	—	47.4	—	78 (4,5)	—	—
-40°	—	47.1	52.1	—	66.4	74.3
-44°	53.6	—	—	—	—	—
-50°	—	—	51.8	76.4 (6)	—	—
-67°	—	45.3	—	—	—	—
-100°	—	—	50.9	—	—	—
-103°	51.9	—	—	—	—	—
-132°	—	—	48.1	—	—	—

The difference in the structures of SF<sub>4</sub>·N(CH<sub>3</sub>)<sub>3</sub> and SF<sub>4</sub>-Et<sub>2</sub>O or SF<sub>4</sub>-THF is interesting, but is not at the same time easy to account for.

In trigonal bipyramidal molecules, e.g., PF<sub>5</sub>, R<sub>2</sub>PF<sub>3</sub> etc., the axial P-F bonds are longer than the equatorial bonds.<sup>7</sup> Muettterties *et al.*<sup>8</sup> have reported that in such molecules the coupling constant J<sub>PF</sub> for the axial bond is smaller than that of the equatorial bond. The interaction between SF<sub>4</sub> and a nucleophile, *viz.*, ether and THF etc. would cause the electron density on the S atom of SF<sub>4</sub> to increase which would probably in turn result in lengthening of the S-F bond. The small difference between the coupling constant of SF<sub>4</sub> and that of SF<sub>4</sub>-Et<sub>2</sub>O shows that the S-F bond lengths of SF<sub>4</sub>-Et<sub>2</sub>O are not much different

from those of  $SF_4$ . It is therefore suggested that the interaction between  $SF_4$  and ether is weak. However, the appreciable decrease in the  $J_{FF}$  of the  $SF_4$ -THF system indicates that the S-F bonds in  $SF_4$ -THF are probably longer than S-F bonds in  $SF_4$ , indicating a stronger interaction between  $SF_4$  and THF. The fact that the  $F^{19}$  resonance signal of  $SF_4$ -THF splits up into two resonances at a higher temperature than that of  $SF_4$ - $Et_2O$  (Figs. 1 and 2) also indicates that the interaction between  $SF_4$  and THF is stronger than between  $SF_4$  and ether. The foregoing conclusion is consistent with the fact that THF<sup>9,10</sup> is more basic than ether.

### References

1. E.L. Muetterties, U.S. Pat. 2,897,055, July 28th, 1959.
2. F. Brown and P.L. Robinson, J. Chem. Soc. 3147 (1955); J.H. Simons, *Fluorine Chemistry* (Academic Press, New York, 1964.) Vol. V.
3. E.H. Rodd, *Chemistry of Carbon Compound: Heterocyclic* (Elsevier Publishing Company, 1957) Vol. IVA, p. 163.)
4. F.A. Cotton, J.W. George and J.S. Waugh J. Chem. Phys., **28**, 994 (1958).

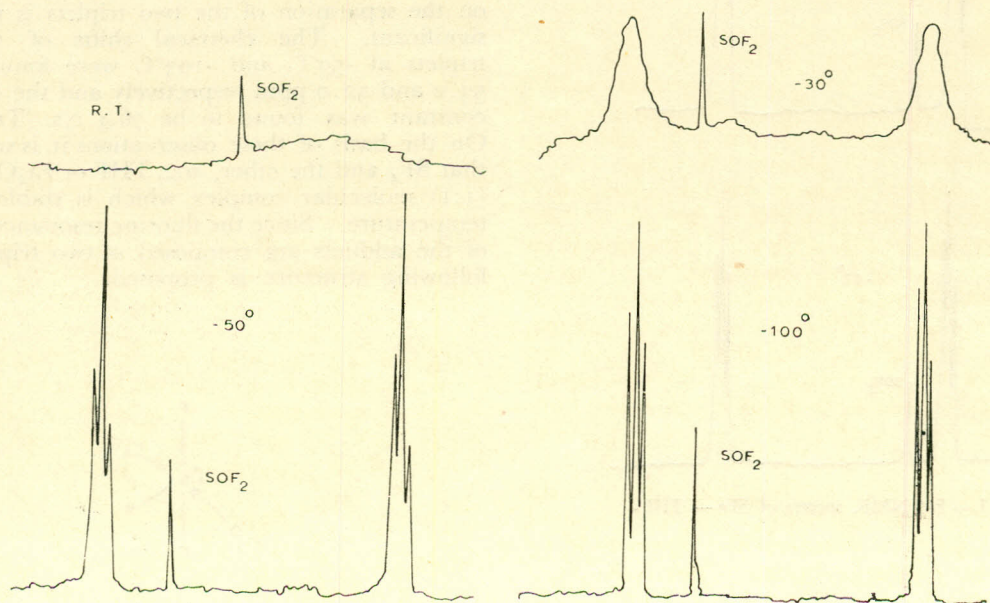


Fig. 2.— $F^{19}$  NMR spectra of  $SF_4$ -ether.

Recently Muetterties<sup>11</sup> has reported the *cis* and *trans* isomer complexes of the metal(IV) fluorides such as  $TiF_4$ ,  $ZrF_4$  and  $SnF_4$  etc. but so far this type of isomerism has not been reported for the complexes of the sulphur-group tetrafluorides. It is suggested that an NMR study of  $MF_4$  (M-S, Se or Te) solution in amines and amides of varying strengths would provide conclusive evidence regarding the *cis* and *trans* complexes of  $SF_4$ ,  $SeF_4$  and  $TeF_4$ .

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5. E.L. Muetterties and W.D. Phillips, J. Am. Chem. Soc., **81**, 1084 (1959).
6. J.W. Quail, unpublished results.
7. R.J. Gillespie and R.S. Nyholm, Quart. Rev. **11**, 339 (1957).
8. E.L. Muetterties, W. Mahler and R. Schmutzer, J. Inorg. Chem., **2** (3), 613 (1963).
9. H.C. Brown and K. Wade, J. Chem. Soc. 1516 (1957).
10. D.E. McLaughlin, M. Tammers and S. Scott, Jr., J. Am. Chem. Soc., **82**, 5624 (1960).
11. E.L. Muetterties, J. Am. Chem. Soc., **82**, 1082 (1960).