ions also were found in relative abundances of 1% and 32%, respectively.

The nuclear magnetic resonance spectra for the SF_5 groups of the addition compounds from reactions 1 through 5 and of F_5SOSF_5 from reaction 6 have been discussed in detail by Merrill, Williamson, Cady, and Eggers.[12] The spectra due to the fluorine atoms attached to carbon add evidence for the proposed structures. The C–F resonance in SF_5OCH_2CHClF was observed to be a doublet, each part of which was further split into a triplet, the splitting being due to the fluorine–hydrogen nuclear interaction. Likewise for $SF_5OCH_2CH_2F$, the C–F resonance was a triplet, each part of which was further split into a triplet. The previously reported values of the fluorine–hydrogen spin–spin coupling constants[13] in CH_3CH_2F are 60 and 20 c.p.s., respectively, between the fluorine and the methylene and methyl protons. The corresponding coupling constants for SF_5OCH_2CHClF are 50 and 18 c.p.s., and for $SF_5OCH_2CH_2F$ are 51 and 23 c.p.s., ±2 in both cases.

No nuclear interaction was observed between the hydrogen atoms on either carbon or the fluorine atoms on the second carbon from the oxygen and the fluorine atoms of the SF_5 group. The splitting between fluorine atoms attached to the carbon atom bonded directly to oxygen and the equatorial and apical fluorine atoms of the SF_5 group was of the order of 9 and 3 c.p.s., respectively.

The approximate chemical shifts between the four equatorial fluorine atoms of the SF_5 group and the fluorine atom(s) bound to carbon (the latter fluorine resonances always appeared at the higher field strength) for a particular compound at 40 Mc. were 8150, 6400, 5530, 11380, and 8350 c.p.s., respectively, for $C_5F_9OSF_5$, $C_2F_5OSF_5$, $FC_2Cl_4OSF_5$, $FC_2H_4OSF_5$, and $FClC_2H_3OSF_5$.

The n.m.r. spectrum of the last of these substances indicated that SF_5OF had added stereospecifically to vinyl chloride.

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

[13] H. S. Gutowsky, L. H. Meyer, and D. W. McCall, *J. Chem. Phys.*, **23**, 982 (1955).

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Iminosulfur Oxydifluoride and Poly-(oxofluorosulfur nitride)

BY G. W. PARSHALL, RICHARD CRAMER, AND R. E. FOSTER

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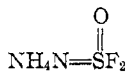
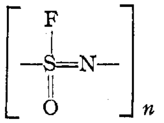
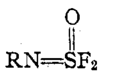
The synthesis and properties of iminosulfur oxydifluoride, $HN{=}SOF_2$, are described. When dehydrofluorinated, this compound yields the rubbery poly-(oxofluorosulfur nitride), which also is directly obtainable from ammonia and sulfur oxytetrafluoride.


$NH_4N{=}\overset{\overset{O}{\|}}{S}F_2$

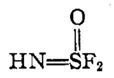
(I)


$\left[-\overset{\overset{F}{|}}{\underset{\underset{O}{\|}}{S}}{=}N-\right]_n$

(II)


$RN{=}\overset{\overset{O}{\|}}{S}F_2$

(III)


$HN{=}\overset{\overset{O}{\|}}{S}F_2$

(IV)

A brief account has been given by Seel and Simon[1] of the reaction of ammonia with sulfur oxytetrafluoride to give the ammonium salt of iminosulfur oxydifluoride (I) and poly-(oxofluorosulfur nitride) (II). The reaction of primary amines with sulfur oxytetrafluoride to give a series of N-alkyl- or N-aryliminosulfur oxydifluorides (III) has been described in greater detail.[2] The synthesis and properties of unsubstituted iminosulfur oxydifluoride (IV) are reported in this paper together with details of the

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

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

preparation and properties of poly-(oxofluorosulfur nitride).

Iminosulfur oxydifluoride was prepared from ammonia and sulfur oxytetrafluoride in the presence of sodium fluoride. The reaction was preferably run in diethyl ether, and the immediate product was an azeotrope containing about 45 mole % ether. Iminosulfur oxydifluoride could be distilled from the azeotrope following the addition of sufficient boron trifluoride to neutralize the ether.

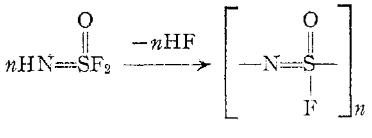
$$\mathrm{NH_3 + SOF_4 + 2NaF} \xrightarrow{(\mathrm{C_2H_5})_2\mathrm{O}} \mathrm{HN{=}SOF_2\cdot 0.85(C_2H_5)_2O + 2NaHF_2} \quad (1)$$

$$\mathrm{HN{=}SOF_2\cdot 0.85(C_2H_5)_2O + BF_3} \longrightarrow \mathrm{HN{=}SOF_2 + BF_3\cdot O(C_2H_5)_2} \quad (2)$$

Iminosulfur oxydifluoride is a colorless liquid which boils at 43° and freezes at about −33°, $n^{25}\mathrm{D}$ 1.3219, $d^{25}{}_4$ 1.5216. The infrared spectrum contains a sharp band at 2.8 μ, assignable to the NH group, strong bands at 7.0 and 8.2 μ, assignable to the N=S=O group, and a strong broad absorption centered at 11.9 μ, assignable to SF bonds. The $\mathrm{F^{19}}$ n.m.r. absorption is a single sharp peak in the S–F region. The proton resonance is an extremely broad band centered in the same region as that for the aromatic hydrogen of toluene. On the basis of these properties and the elemental analysis, structure IV has been assigned.

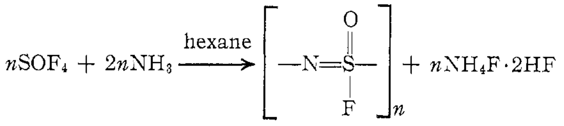
The iminosulfur oxydifluoride–ether azeotrope is a colorless liquid which boils at 57.5°. Elemental analyses correspond to the composition $\mathrm{HNSOF_2\cdot[(C_2H_5)_2O]_{0.85}}$. The liquid appears to be an azeotrope rather than an ether complex because the molecular weight (cryoscopic, in benzene) is only 93, which indicates complete dissociation. No evidence for complex formation was found in the infrared spectrum. The proton magnetic resonance contained a single, broad peak in the NH region in addition to the peaks assignable to ether. The $\mathrm{F^{19}}$ nuclear magnetic resonance was a single peak in the SF region.

Dehydrofluorination of iminosulfur oxydifluoride yields a rubbery polymer of oxofluorosulfur nitride.



$$n\mathrm{HN{=}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{F_2} \xrightarrow{-n\mathrm{HF}} \left[-\mathrm{N{=}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{F}}{|}}{\mathrm{S}}}- \right]_n \quad (3)$$

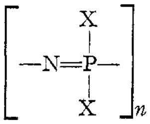
If sulfur oxytetrafluoride is treated with ammonia the polymer is obtained in one step,[3] as in eq. 4.



$$n\mathrm{SOF_4} + 2n\mathrm{NH_3} \xrightarrow{\text{hexane}} \left[-\mathrm{N{=}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{F}}{|}}{\mathrm{S}}}- \right]_n + n\mathrm{NH_4F\cdot 2HF} \quad (4)$$

The infrared spectrum of the polymer contains absorption bands attributable to N=S=O (7.4 and 8 μ) and to S–F (12 μ).

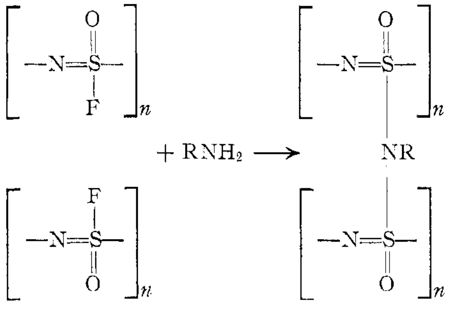
The $\mathrm{F^{19}}$ nuclear magnetic resonance of a concentrated solution of the polymer in phosphorus oxychloride appeared as a single peak in the SF region. No proton magnetic resonance could be observed. These facts together with the elemental analysis support structure II.



$$\left[-\mathrm{N{=}}\overset{\overset{\mathrm{X}}{|}}{\underset{\underset{\mathrm{X}}{|}}{\mathrm{P}}}- \right]_n$$

(V)

The resemblance to the rubber-like phosphorus halonitrile polymer (V) is apparent. Both are chains of nitrogen and negatively substituted tetrahedral atoms, and, in fact, in the case where X is fluorine, they are isoelectronic. Poly-(oxofluorosulfur nitride) appears to be more stable toward hydrolysis than are the phosphorus halonitrile polymers. It is not affected by cold aqueous ammonia or water or by 6% sulfuric acid at 100° for at least 3 hr., but rapidly disintegrates in 5% sodium hydroxide at 100°. The sulfur–fluorine bond also is readily attacked by nitrogen bases at elevated temperatures, so that polymer prepared directly from ammonia and sulfur oxytetrafluoride may be crosslinked to some extent through nitrogen atoms.



$$\begin{array}{c} \left[-\mathrm{N{=}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{F}}{|}}{\mathrm{S}}}- \right]_n \\ \left[-\mathrm{N{=}}\overset{\overset{\mathrm{F}}{|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}- \right]_n \end{array} + \mathrm{RNH_2} \longrightarrow \begin{array}{c} \left[-\mathrm{N{=}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}- \right]_n \\ | \\ \mathrm{NR} \\ | \\ \left[-\mathrm{N{=}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}- \right]_n \end{array}$$

The use of cesium fluoride as dehydrofluorinating agent gives a particularly clean polymer. Polymerization was accomplished by refluxing a mixture of the salt and a benzene solution of iminosulfur oxydifluoride or its ether azeotrope

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[3] R. Cramer, U. S. Patent 3,017,240, January 16, 1962.

for several hours. After the precipitated polymer was washed with methanol, it was isolated as a white, tough rubber which could be pressed to opaque films at 100° and 1500 p.s.i. In contrast to the partially crosslinked polymer obtained by direct reaction of ammonia and sulfur oxytetrafluoride, this product is completely soluble in phosphorus oxychloride or dimethylformamide. It has an inherent viscosity of 0.7, corresponding to a minimal molecular weight of 20,000. It melted to a viscous liquid at 110–120°. The infrared spectrum contained extremely broad bands in the 6–9 and 11–14 μ regions assignable to the N═S═O and SF functions, respectively.

Experimental

Synthesis of Iminosulfur Oxydifluoride–Ether Azeotrope.—A mixture of 105 g. (2.5 moles) of sodium fluoride and 500 ml. of ether was cooled to −80° and 125 g. (1 mole) of sulfur oxytetrafluoride was added. The solution was warmed to −35° and 14 g. (0.8 mole) of ammonia was introduced at the rate of 3 ml./sec. at that temperature. The mixture then was distilled at atmospheric pressure. The portion boiling up to 40° was discarded. Fractions boiling at 40–50° (42 g.) and 50–55° (66 g.) were collected. Chromatographic analysis showed about 12% iminosulfur oxydifluoride in the second fraction and 50% in the third. The total yield of iminosulfur oxydifluoride was 53 g. (53% based on sulfur oxytetrafluoride or 67% based on ammonia). Temperature control during ammonia addition was critical, as lower temperatures promoted plugging of the inlet tube and greater solids formation.

An azeotrope fraction which boiled at 57.7° had a composition corresponding to $HNSOF_2 \cdot [(C_2H_5)_2O]_{0.85}$.

Anal. Calcd. for $HNSOF_2 \cdot [(C_2H_5)_2O]_{0.85}$: C, 24.71; H, 5.80; F, 23.23; N, 8.58; S, 19.63. Found: C, 25.28, 25.56; H, 6.25, 6.00; F, 24.30, 22.17; N, 9.40, 8.82; S, 19.66, 19.43.

When methylene chloride was used as the reaction medium, an azeotrope containing 34% iminosulfur oxydifluoride, which distilled at 33.5°, was obtained.

Isolation of Iminosulfur Oxydifluoride.—A 150-ml. stainless steel cylinder was charged with 47 g. of iminosulfur oxydifluoride–ether azeotrope (containing 0.29 mole of iminosulfur oxydifluoride) and 19 g. (0.28 mole) of boron trifluoride and allowed to stand for 24 hr. Distillation of the mixture gave 24.5 g. (84%) of iminosulfur oxydifluoride, b.p. 43°. It is important not to use an excess of boron trifluoride for it appears to form a nonvolatile complex with iminosulfur oxydifluoride.

Anal. Calcd. for $HNSOF_2$: N, 13.86; S, 31.72; F, 37.59. Found: N, 14.46; S, 32.45; F, 37.96.

Poly-(oxofluorosulfur nitride) from Sulfur Oxytetrafluoride and Ammonia.—A solution of 11.2 g. (0.09 mole) of sulfur oxytetrafluoride in 250 ml. of hexane was stirred vigorously and maintained at −70° in a nitrogen atmosphere as 1.7 g. (0.01 mole) of ammonia was added over a period of 10 min. A white precipitate formed during the addition, and the mixture was allowed to warm to room temperature over a period of 2 hr. The supernatant liquid was decanted, and the solid residue was washed with water to leave a tough elastic polymer.

Anal. Calcd. for SNOF: S, 39.55; N, 17.28; F, 23.44. Found: S, 39.82; N, 18.08; F, 23.67.

Poly-(oxofluorosulfur nitride) from Iminosulfur Oxydifluoride and Cesium Fluoride.—A slurry of 35 g. (0.25 mole) of anhydrous cesium fluoride in 50 ml. of benzene was stirred while 5.5 g. (0.055 mole) of iminosulfur oxydifluoride was added. An exothermic reaction occurred, and the temperature of the mixture rose to 40°, then fell to 30°, over a period of 1 hr. The mixture was boiled under reflux for 1 hr., and the supernatant liquid decanted. The residual solid was washed with water to leave white, tough, elastic poly-(oxofluorosulfur nitride).

Iminosulfur oxydifluoride–ether azeotrope also can be converted into poly-(oxofluorosulfur nitride) by refluxing a solution in benzene with cesium fluoride.

Anal. Calcd. for SNOF: S, 39.55; N, 17.28. Found: S, 38.19; N, 17.03.