Reaction of Hexafluoropropene with Sulfur[1]

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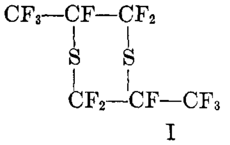
Received May 21, 1956

Reports in the literature of fluorocarbon derivatives containing the typical monosulfide linkage are quite limited. Hauptschein and Grosse[2] in their preparation of the polysulfides $(C_3F_7)_2S_2$ and $(C_3F_7)_2S_3$ reported the formation of a trace of a compound that was thought to be $(C_3F_7)_2S$, but no identification was made. Haszeldine[3] prepared $(CF_3)_2S$ from the disulfide, $(CF_3)_2S_2$, by prolonged ultraviolet irradiation and found it to be quite stable to hydrolysis and unreactive in the usual organic sulfide reactions. In contrast, the fluorocarbon polysulfides are easily and completely hydrolyzed by dilute alkali.

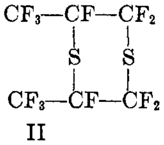
Since the fluorocarbon monosulfides seem to approach the extreme stability of the fluorocarbon oxides and the fluorocarbon nitrides, interest has developed in synthesis of compounds containing this structural feature in order that their properties might be more fully studied.

Pyrolysis of n-C_3F_7COONa with an excess of sulfur at 300° produced a variety of products from which was separated a liquid fraction boiling at 112–113°. The molecular weight and analysis of this compound indicate an empirical formula $C_6F_{12}S_2$. The heterocyclic formula I or II is proposed



I

or



II

since this structure might result from the reaction of sulfur with $CF_3CF{=}CF_2$, known to be formed by pyrolysis of n-C_3F_7COONa.[4]

Reaction of hexafluoropropene, $CF_3CF{=}CF_2$, with an excess of sulfur produces, in higher yield, a compound with the same characteristics as the compound isolated from the pyrolysis of n-C_3F_7COONa in the presence of sulfur. This reaction supports the dithiane structure proposed above. The infrared absorption spectra of the compound prepared in this manner is shown in Figure 1. The disulfide structure is ruled out since this compound is stable to prolonged refluxing in aqueous alkali, whereas fluorocarbon polysulfides are easily hydrolyzed. This heterocyclic fluorocarbon is practically insoluble in water, alcohol, and carbon disulfide but soluble in a variety of solvents such as acetic acid, benzene, acetone, and carbon tetrachloride.

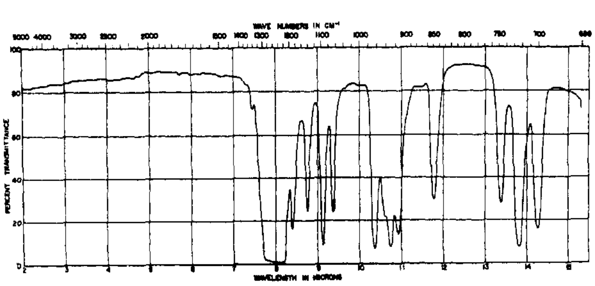


FIG. 1. INFRARED ABSORPTION SPECTRUM OF BIS(TRIFLUOROMETHYL)PERFLUORODITHIANE

EXPERIMENTAL

Pyrolysis of sodium heptafluorobutyrate in presence of sulfur. A mixture of 118 g. (0.5 mole) of sodium heptafluorobutyrate and 100 g. of sulfur was thoroughly mixed by grinding together in a dry atmosphere and the mixture was placed in a steel reaction vessel of 300-ml. capacity. The reactants were dried under vacuum at 120° for 1 hr.; the reactor was then sealed and heated to 300° for 12 hr. When the reactor had cooled to 160°, the total volatile reaction product was transferred through the vacuum system to a liquid air trap, and the trap was removed from the vacuum system and allowed to warm to room temperature. Volatile gases from the reaction product were retained in a Dry Ice–acetone cooled trap and identified as unreacted $CF_3CF{=}CF_2$ [5 g., mol. wt. 152 (Dumas)]. The remaining reaction product was refluxed with excess 10% sodium hydroxide solution for 18 hr., the water-insoluble layer separated and dried with anhydrous calcium chloride. Fractional distillation at atmospheric pressure gave 2 g., b.p. 112.0–113.0°; 16 g., b.p. 113.0–113.5° (mostly 113.0) n_D^{25}, 1.3390, 5 g. residue and column hold up.

Anal. Calcd. for $C_6F_{12}S_2$: C, 19.8; S, 17.6; mol. wt., 364. Found: C, 19.9; S 17.3; mol. wt., 366.

Reaction of hexafluoropropene with sulfur. Sulfur (130 g.) was placed in a steel reaction vessel of 300-ml. capacity, the vessel was evacuated and 117 g. (0.78 mole) $CF_3CF{=}CF_2$ was added through the vacuum system. The reactor was sealed and heated at 300° for 36 hr., then cooled to room temperature and the volatile product removed. Fractionation at atmospheric pressure gave the following cuts: (1) 19 g., b.p. 26.5–109.0 (not yet identified but distillation shows two flats at 46° and 55°); (2) 18 g., b.p. 109–112.8 (mostly 112.8); and (3) 68 g., b.p. 112.8–113.5. Fraction 3 (30 g.) was freed of traces of sulfur halides by refluxing with 10% sodium hydroxide for 18 hr., washed with water, and dried with calcium chloride. Fractionation gave (1) 2 g., b.p. 112.8–113.0; (2) 19 g., b.p. 113.0–113.3; (3) 2 g., b.p. 113.3–113.8, residue, 2 g.

Anal.[5] Fraction 2., C, 20.4; S, 17.1; mol. wt., 363; n_D^{25} 1.3406; d^{25}, 1.762. Calcd. for $C_6F_{12}S_2$, C, 19.8; S, 17.6; mol. wt., 364.

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[1] This work was supported in part by the Office of Naval Research under Contract N-Onr 580(03); NR 356-333 with the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 5461 (1951).

[3] R. N. Haszeldine, *J. Chem. Soc.* 2198 (1952).

[4] J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.*, **75**, 4525 (1953).

[5] Molecular weights by Victor Meyer method. Carbon and sulfur analyses by Peninsular Chemical Research, Gainesville, Fla.