

reflect that with these olefins the stability constants for silver ion complexes depend on ionization potential of the donor<sup>19c</sup> to a different degree or in a different way than do those for iodine complexes. Or the lack of parallel trends may indicate a difference in structure for the two types of complexes.

The silver ion-olefin complex has been described<sup>21</sup> in terms of some donation of electrons (charge-transfer) by overlapping of the occupied d-orbitals of silver ion with the unoccupied antibonding  $\pi$ -orbital of the olefin as well as charge-transfer by overlapping of the occupied  $\pi$ -orbital of the olefin with the unoccupied s-orbital of silver ion. Energy contributions from d-orbital overlapping are probably small compared with  $\pi$ -s-orbital overlapping.<sup>22</sup> One might well expect that this contribution would be considerably more important with silver ion, with its "exposed" d-orbitals, than with iodine molecule, with relatively unexposed d-orbitals. The p-orbitals of iodine do not have the appropriate geometry for overlap

(21) M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).

(22) Qualitative estimate by Dr. S. P. McGlynn, Louisiana State University; private communication.

with the antibonding  $\pi$ -orbital of the olefin. Since the energy contributions from d-orbital overlap are expected to be small, they will become important or recognizable only when the contributions from  $\pi$ -s-orbital overlap become small. That is, this difference in structure for the two types of complexes may result in different orders for stability constants only among relatively weak donors. The olefins used in this study are weaker donors than are aromatic hydrocarbons.

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BATON ROUGE, LA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, UNIVERSITY OF FLORIDA]

## Some New Sulfur-bearing Fluorocarbon Derivatives<sup>1,2</sup>

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Further studies involving sulfur-bearing organic materials by the electrochemical process in HF are herein reported. New starting materials such as trithiane, bis-1,2-meththioethane and dimethyl disulfide were investigated. Thioxane, studied previously, was investigated on a larger scale with some novel results, which cast some further light on the many ramifications of the process. Such new compounds as  $\text{CF}_3\text{SF}_4\text{CF}_2\text{SF}_6$ ,  $\text{CF}_3\text{SF}_4\text{C}_2\text{F}_4\text{SF}_6$ ,  $(\text{C}_2\text{F}_4\text{SF}_4)_2$ ,  $(\text{CF}_2\text{SF}_4)_3$  and  $\text{C}_2\text{F}_5\text{SF}_4\text{CF}_3$  were isolated and identified and several reported compounds such as  $\text{C}_2\text{F}_5\text{OC}_2\text{F}_4\text{SF}_6$ ,  $\text{C}_2\text{F}_4\text{OC}_2\text{F}_4\text{SF}_6$  and  $\text{SF}_6\text{CF}_2\text{SF}_6$  were

obtained with high purity and their simple properties are noted. Whenever it was feasible, the isolable products from the various investigations were purified by vapor phase chromatography and structures were confirmed by nuclear magnetic resonance (n.m.r.) spectral analysis.

### Introduction

The electrochemical (Simons) process is one of the major methods for preparing certain types of fluorocarbon materials. Although it has definite limitations it also manifests definite preparatory advantages. The preparation, by this process, of several simple derivatives of  $\text{SF}_6$  have been reported<sup>3</sup> in recent years. The purpose of this work was to determine the feasibility of preparing fluorocarbon sulfides with so-called "polyfunctional" character. However, it will be noted that although several products of this nature were isolated and identified, their yields were limited by the tendency of the process to fragment, regroup frag-

ments, cyclize and decyclize the original chain structure.

Vapor phase chromatography and nuclear magnetic resonance spectroscopy have been used as extensively as possible for purity determinations and structure analysis. They have been most useful in conjunction with classical analytical methods, for confirming the character of the isolable products. However, they still manifest certain limitations as analytical tools which await the accumulation of the needed background data.

### Experimental

The electrochemical unit used in this work was not unlike that described by Hoffmann and Simmons<sup>3d</sup> and designated by them cell C. There were only minor differences in design. The overhead condenser was cooled directly by an expanding refrigerant (Freon 12) from a standard refrigeration machine, and the superheat from this expansion was used to cool a water-bath in which the cell was immersed, before the gas was returned to the high pressure side of the compressor. In general, the condenser was maintained between  $-20$  and  $-30^\circ$  and the bath between  $17$  and  $19^\circ$ . The area of each electrode system was about  $1,000$  sq. cm.

Vapor phase chromatographic studies were made with a Perkin-Elmer Fractometer, model 154, using such stationary phases as are noted in the text. Bulk separations were performed in packed one inch tubes, 2 or 4 meters long, using

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(2) This work was supported by the Chemistry Branch, Office of Naval Research, and any or all of this paper may be reproduced for purposes of the United States Government.

(3) (a) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953); (b) W. A. Severson, T. J. Brice and R. I. Coon, 128th Meeting A.C.S., Minneapolis, Minn., September 11-16, 1955, Div. Ind. & Eng. Chem., Fluorine Chem. Subdivision; (c) R. Dresdner, *THIS JOURNAL*, **79**, 69 (1957); (d) F. W. Hoffman, T. C. Simmons and co-workers, *ibid.*, **79**, 3424 (1957).

TABLE I  
 PROPERTIES OF COMPOUNDS ISOLATED FROM SULFUR-BEARING STARTING MATERIALS

Compound	Source <sup>a</sup>	B.p., °C.	F.p., °C.	$n_D^{25}$	$d_4^{25}$	Estd. purity, wt. %	Prior reference
CF <sub>3</sub> SF <sub>5</sub>	I, II, IV	-20.8				99	3a
SF <sub>5</sub> CF <sub>2</sub> SF <sub>5</sub>	I	59.6-59.7		1.2884	2.041	99	3a, 6
CF <sub>3</sub> SF <sub>4</sub> CF <sub>2</sub> SF <sub>5</sub>	I	87.8-88.1		1.3010		90	
(CF <sub>2</sub> SF <sub>4</sub> ) <sub>3</sub>	I	144.1-144.5		1.3258	2.162	99.5?	
CF <sub>3</sub> SF <sub>4</sub> C <sub>2</sub> F <sub>5</sub>	II	47.1		1.2674	1.803	99.9	
C <sub>2</sub> F <sub>5</sub> SF <sub>4</sub> C <sub>2</sub> F <sub>5</sub>	II	70.0-70.5		1.2752		99.9	3c, 3d
CF <sub>3</sub> SF <sub>4</sub> C <sub>2</sub> F <sub>5</sub> SF <sub>5</sub>	II	112.0-112.5		1.3041	2.002	95	
(C <sub>2</sub> F <sub>4</sub> SF <sub>4</sub> ) <sub>2</sub>	II	82 (61 mm.)	76-76.5				
C <sub>2</sub> F <sub>5</sub> OC <sub>2</sub> F <sub>5</sub>	III	2 (3 mm.)				95	8
C <sub>2</sub> F <sub>5</sub> SF <sub>5</sub>	III	13.2-14.2				95	3c, 3d
C <sub>2</sub> F <sub>5</sub> OC <sub>2</sub> F <sub>4</sub> SF <sub>5</sub>	III	65°		1.2598	1.772	98.5	3b
C <sub>2</sub> F <sub>4</sub> OC <sub>2</sub> F <sub>5</sub> SF <sub>5</sub>	III	80.3	17.1-17.3	1.3041	1.9031	99.5-99.7	3b, 3d
CH <sub>3</sub> SF <sub>5</sub> + CH <sub>3</sub> SF <sub>4</sub> CH <sub>2</sub> F (mixture)	IV	28.3	-18.7		1.65 <sup>b</sup>	73/27 <sup>c</sup>	

<sup>a</sup> I, *s*-trithiane; II, bis-1,2-meththioethane; III, thioxane; IV, methyl disulfide. <sup>b</sup> Approximate. <sup>c</sup> Wt. ratio.

helium or nitrogen as a developer. This equipment will be described in another place.<sup>4</sup>

Nuclear magnetic resonance spectra were obtained on Varian Associates equipment using a 40 mc. probe and CF<sub>3</sub>-COOH as a reference standard.<sup>5</sup>

**Cell Operation.**—In general, operation of the cell was conducted as uniformly as possible. Direct current power was supplied by a Mallory 6RS25-1 rectifier and the voltage was maintained as low as possible, compatible with an average current of 9-13 amp. The head of the electrochemical unit was provided with sufficient entry and exit ports to allow HF and starting material to be added at necessary intervals, to remove high boiling products from the bottom of the unit and to allow for the escape of hydrogen gas and low boiling products. The existing gases and vapors were passed through a train consisting of a blow out device with a head of 10 cm., lime traps to remove the entrained HF, a P<sub>2</sub>O<sub>5</sub> drying tube, a product trap cooled in Dry Ice-acetone and a wet test meter to measure the non-condensables. In each case a liquid air cooled product trap was placed after the Dry Ice trap for a representative period of time in order to obtain an estimate of the very low boiling products and to correct for hydrogen actually produced. In the case of the operation with trithiane, a solid, an entry port was modified so that starting material could be added through a polyethylene powder funnel. The port was capped after each addition. The conditions of and products from each electrochemical operation are reported separately below.

**Operation with *s*-Trithiane (CH<sub>3</sub>S)<sub>3</sub>.**—The trithiane was purchased from DPI (Eastman), m.p. 214-216°. It was used as shipped. Twenty-five grams (0.18 mole) was added to approximately 800 g. (40 moles) of electrolytically dried HF. A current was passed through the solution until hydrogen gas equivalent to 10 g. of starting material was evolved. Then 15 g. of trithiane was added thereafter for every 50 l. of hydrogen gas metered at room conditions until 470 g. (3.4 moles) had been added, and the charge completely used up. The average operating characteristics were 4.3 ± 0.1 volts and 8.2 amp. for 107 faraday. Eleven hundred liters of hydrogen gas were metered at room temperature. The Dry Ice condensate amounted to 360 g. of product while the estimated total liquid air condensate was in the order of 800 g. Two hundred and fifty grams of crude product was removed from the cell. This "cell product" was separated from a small amount of HF layer with a polyethylene separatory funnel. A solid phase denser than the HF phase and lighter than the fluorocarbon phase was also encountered. This was removed, dried and proved to be elemental sulfur. It amounted to more than 20 g. The fluorocarbon phase was washed with dilute base several times and dried.

The Dry Ice condensate, after being dried over P<sub>2</sub>O<sub>5</sub> *in vacuo*, formed two liquid phases at -80°. The top shim-

mering layer was pipetted off and was found to boil between 46.1 and 46.3°. It had a mol. wt. of 77 and a  $n_D^{25}$  of 1.6290, the proximate properties of CS<sub>2</sub>; 25 g. was isolated.

The residual products from all sources, amounting to about 500 g. of fluorine-containing materials, were fractionated in appropriate equipment and the indicated quantities of more or less pure materials were isolated and identified: 1. CF<sub>3</sub>SF<sub>5</sub>, b.p. -21 to -20°, mol. wt. 195-197; 99% by wt. as determined by chromatographic analysis on a stationary phase of the ethyl ester of Kel-F acid 8114 at room temperature. A stationary phase of dibutyl phthalate gave the same results. The infrared spectrum agreed with that of samples from this Laboratory and that reported in the literature.<sup>3a</sup> This amounted to 90 g.

2. The next fractionation flat appeared at 59.6-59.7° and proved to be SF<sub>5</sub>CF<sub>2</sub>SF<sub>5</sub>. This is not an unreported compound,<sup>3a, 6</sup> but some of its properties have not been reported.

*Anal.* Calcd. for CF<sub>2</sub>S<sub>2</sub>: F, 74.8; S, 21.1; mol. wt., 304. Found: F, 75.0, S, 20.9; mol. wt., 303;  $n_D^{25}$  1.2884;  $d_4^{25}$  2.041.

The analytical sample was better than 99% pure chromatographically and the structure was confirmed by n.m.r. analysis. The spectrum showed three lines at the positions characteristic for CF<sub>2</sub>, F-SF<sub>4</sub>-C and SF<sub>4</sub>-C. The fraction amounted to 55 g.

3. Finally a fraction was isolated at 144.1-144.5° which seems to have the proper properties for perfluoro-*s*-trithiane dodecafluoride, (CF<sub>2</sub>SF<sub>4</sub>)<sub>3</sub>, but oddly had a m.p. below -80°. The purity of the fraction was checked chromatographically on a stationary phase of Kel-F grease at 130° and the evidence was for a purity of about 99.5%, although the main peak was quite broad and could have hidden at least isomeric impurities. The n.m.r. spectrum had one line in the CF<sub>2</sub> region and 3 main lines in the S-F region with intensities of 3:2:1: indicating that the fluorines on the sulfur are not magnetically equivalent.<sup>7</sup> Weak impurity lines also were reported<sup>6</sup> in the S-F region implying that the chromatographically ascertained purity was somewhat questionable.

*Anal.* Calcd. for C<sub>3</sub>F<sub>12</sub>S<sub>3</sub>: F, 72.3; S, 20.2, mol. wt., 474. Found: F, 72.5; S, 20.0;  $n_D^{25}$  1.3258;  $d_4^{25}$  2.162; mol. wt. 462 ± 10 (four trials).

The molecular weight cannot be regarded as being too valid since it was done by the Regnault method using a cathetometer to read the pressure of about 6 mm. The isolated fraction amounted to only 28.5 g. and did not appear to be too stable above its boiling point.

Distillation flats were observed in the boiling range of several other predictably possible products, but these were mixtures. For example, 100 g. of product boiling between 5-17° showed several flats with molecular weights between 190-221, at least two liquid phases below -80° and 5 or 6

(4) T. M. Reed, John F. Walter, R. Cecil and R. Dresdner, *in press*.

(5) The authors are indebted to Dr. H. S. Gutowsky, University of Illinois, and Dr. Max T. Rogers, Michigan State University, for the n.m.r. measurements and interpretations.

(6) E. A. Tyczkowski and L. A. Bigelow, *THIS JOURNAL*, **75**, 3523 (1953).

(7) N. Muller, P. C. Lauterbur and G. F. Svatos, *ibid.*, **79**, 1043 (1957).

major components as determined chromatographically. Other flats around 87–88°, 112–114° and 155–156° suggested the presence of isomers of  $C_2S_2F_{14}$ ,  $C_3S_2F_{16}$  and  $C_3S_3F_{20}$ , respectively. These proposed substances did have approximately correct molecular weights, but the first and third were less than 70% one component while the second appeared to have a purity of about 90%. It had an n.m.r. spectrum consistent with the formula  $CF_3SF_4CF_2SF_3$ . The spectrum had three main lines in positions and relative intensities corresponding to  $CF_3S$ ,  $C-SF_4-C$ , and  $C-SF_4-F$ . The  $CF_3$  resonance is a quintet with 22.3 c.p.s. splitting, which implies there is a  $CF_3-SF_4-C$  group. One of the  $SF_4$  lines had 9 well resolved components, probably due to the  $CF_3$ ,  $CF_2$  influences. The two lines from the  $SF_4-F$  were broad and no structure is resolved. This agreed with the results from  $SF_4CF_2SF_3$ . Again there was evidence for impurities. The chemical analytical data bear out the presence of impurities to some extent despite tolerable molecular weights.

*Anal.* Calcd. for  $C_2S_2F_{14}$ : F, 75.1; S, 18.1; mol. wt., 354. Found: F, 76.7; S, 16.7; mol. wt., 350;  $n_D^{25}$  1.3010.

**Operation with Bis-1,2-dimeththioethane,  $CH_3SC_2H_4SCH_3$ .**—Originally, it was intended to use dimercaptoethane,  $HSC_2H_4SH$ , but the process failed to the extent that tars formed on the electrodes blocking the current. This phenomenon is found to occur with substances having a H atom bonded to another atom of either S, O or N. The dimercapto compound was converted to the dimeththio by methylation in aqueous base with methyl sulfate. This product boiled at 63° at 7 mm.

In this operation, 20 g. of the starting material was added to 800 g. of electrolytically dried HF and 10-g. increments were added for every 50 l. of hydrogen gas evolved until a charge of 370 g. (4.1 moles) was run out; HF was added periodically to keep the liquid level near the top of the electrodes. The liquid level was determined by measuring the d.c. resistance between a 1/8" nickel rod and the cell body. The nickel rod fitted snugly in a Teflon gland and could be moved vertically at will. The gland could sustain a positive pressure of 5 p.s.i. without leakage.

Electrical conditions were  $4.4 \pm 0.3$  volts at an average of 10.1 amp. until a total of 109.5 faraday was passed. The hydrogen evolved amounted to 1240 l. at room conditions. The Dry Ice condensate amounted to 670 g. and the cell-retained product to 88 g. The estimated liquid air condensate did not exceed 300 g.

Five separate materials were isolated in reasonably good purity from the products upon fractionation: 1. A fraction boiling at -20.8, mol. wt. 196, amounting to 170 g. proved to be  $CF_3SF_5$ .

2. The next pure fraction was not detected until the column head temperature reached 47.1°. Here a fraction amounting to 90 g. was obtained which after final investigation of its properties proved to be  $C_2F_8SF_4CF_3$ . It boils about 5° higher than its isomer  $C_2F_7SF_5$  and has a considerably different refractive index at 25° than  $C_2F_7SF_5$ ; viz., 1.2594.<sup>3d</sup> It had a relatively simple infrared spectrum with the following band assignments in microns: 6.66v, 6.88v, 7.47ms, 7.90–7.98vs, 8.14vs, 8.40vs, 10.09ms, 11.65–11.75vvs, 12.46s, 13.55–13.63w, 14.37–14.52vs.

Chromatographically, the sample was extremely pure, recording no detectable impurities. The n.m.r. spectrum showed the proper assignments for the proposed structure, the  $\delta$ -values (chemical shift relative to  $CF_3COOH$ ) being +6.3 for  $CF_3C$  (quartet), -9.8 for  $CF_3S$ , -97.3 for  $C-SF_4-C$  and +21.3 for the  $CF_2$  group. This is a different spectrum than that given by Muller, Lauterbur and Svatos<sup>7</sup> for  $C_3F_7SF_5$ .

*Anal.* Calcd. for  $C_3SF_{12}$ : F, 77.03; S, 10.82; mol. wt., 296. Found: F, 77.0; S, 10.97; mol. wt., 297;  $n_D^{25}$  1.2674;  $d_4^{25}$  1.803.

3. At 70.0 to 70.5° a fraction amounting to 28 g. was obtained. From its mol. wt. 346,  $n_D^{25}$  1.2752,<sup>3b,3c</sup> and a comparison infrared spectrum it was shown to be  $(C_2F_5)_2SF_4$ . The sample was 99.3% pure. The n.m.r. spectrum was the same as that previously obtained.<sup>3c,7</sup>

4. At 112.0–112.5° a fraction amounting to 19 g. was obtained. Chromatographically it was about 95% one component. No n.m.r. spectrum was obtained, but from the analysis and boiling point it is assumed to be an isomer of  $C_3S_2F_{16}$  and extrapolating from the structure of the starting material it was probably  $CF_3SF_4C_2F_4SF_5$ .

*Anal.* Calcd. for  $C_3S_2F_{16}$ : F, 75.3; S, 15.75; mol. wt., 404. Found: F, 74.5; S, 15.3; mol. wt., 409;  $n_D^{25}$  1.3042;  $d_4^{25}$  2.022.

5. Finally, a material boiling at 82° at 61 mm. (or 88° and at 83 mm.) which was a solid at room temperature came over in the fractionation. It amounted to 12 g. As the sample was somewhat slushy at room temperature and had a strong sulfurous odor, it was washed successively with dilute base, water and acetone and dried at reduced pressure. The final residue which amounted to about 6 g. had a m.p. of 76–76.5°. From the analysis and the fact it was a high melting solid it was believed to be  $(C_2F_4SF_4)_2$ , the perfluorocyclic analog of the starting material, according to the current nomenclature perfluoro-*s*-dithiane octafluoride.

*Anal.* Calcd. for  $C_4S_2F_{16}$ : F, 73.2; S, 15.4; mol. wt., 416. Found: F, 73.2; S, 15.1.

Only 310 out of some 650 g. of products boiling above -50° were identified.

The intercuts were large and although there were numerous 1° flats in the fractionation between 0 and 30°, none of these fractions was pure enough to warrant investigation. The molecular weights all varied between 180 and 185, indicating partially hydrogenated compounds which in the main seem to be relatively stable to concentrated base.

**Operation with Thioxane,  $O(C_2H_5)_2S$ .**—This operation represented a much more extensive study with thioxane than had been attempted previously.<sup>3b,3d</sup> Again, the starting material was added to electrolytically dried HF at the rate of about 30 g. for every 50 l. of hydrogen gas evolved until a charge of 650 g. (6.25 moles) was used up. The operation was performed at  $4.5 \pm 0.3$  volts and an average of 11.0 amp. until 186 faraday was passed. Some 2050 l. of hydrogen was formed. The Dry Ice condensate amounted to 612 g. and 942 g. of crude product was obtained from the cell. The cell products were cleaned with base and dried before fractionation. Four main products were isolated and identified. 1. One hundred and sixty-four grams of  $(C_2F_5)_2O$  was isolated at 2–3°. This was identified from its boiling point, mol. wt. 255, and the comparison infrared spectrum.<sup>8</sup>

2. Sixty-seven grams of  $C_2F_8SF_5$  was isolated at 13.2–14.2° and were identified from the boiling point, mol. wt. 245, and a comparison infrared spectrum.

3. Between 67.5 and 68.5°, 105 g. of material was isolated with a fairly constant refractive index of 1.2627–1.2635 at 25°. Chromatographically the main component varied in purity from 85 to 92% by weight. This material was purified in the large scale vapor chromatographic unit over a hexadecane stationary phase at the rate of 2 g. per charge per 20 min. at 45° using nitrogen gas as a developer. The main component was collected in a Dry Ice trap by observing the chromatogram on a Brown recorder. All of the fractions thus treated proved to be 98.5% pure as determined with the Perkin-Elmer refractometer on a Kel-F ester column. This material proved to be  $C_2F_5OC_2F_4SF_5$  previously reported.<sup>3b</sup>

*Anal.* Calcd. for  $C_4F_{14}SO$ : F, 73.4; S, 8.84; C, 13.35; mol. wt., 362. Found: F, 73.3; S, 9.00; C, 13.54; mol. wt., 360;  $n_D^{25}$  1.2598;  $d_4^{25}$  1.772.

4. Finally a series of fractions were obtained which boiled between 78.8° and 81° and amounted to 445 g. Chromatographically the purity of the major components varied from 69 to 97% as the refractive index rose from 1.2990 to 1.3032. These fractions were purified by large scale vapor chromatography using two stationary phases of dibutyl phthalate and hexadecane in series each on Celite in 1" tubes 2 meters long. Four-gram samples were used per charge per 35-min. interval. Helium was used as the developer gas at a flow rate of 1.5 SCFH. The purity of the final product thus treated was between 99.5 and 99.7%. This product was perfluorothioxane tetrafluoride,  $C_2F_4OC_2F_4SF_4$ , previously

reported.<sup>3b,3d</sup> The purified material had the following simple physical properties, b.p. 80.3°, m.p. 17.1–17.3°,  $n_D^{25}$  1.3041 and  $d_4^{25}$  1.9031.

The n.m.r. spectrum agreed with that determined by Muller, Lauterbur and Svatos<sup>7</sup> on the sample prepared by Hoffmann and Simmons.<sup>3d</sup>

(8) "Fluorine Chemistry," J. H. Simons, Editor, Academic Press, Inc., Vol. II, New York, N. Y., 1955, p. 479.

The 1556 g. of crude product from this operation was reduced to 1322 g. on treatment with base. Besides the 720 g. of identified products and the numerous large intercuts, above 165 g. of material boiled well over 85° but this latter material showed variable refractive index and purity with a tendency to decompose during the fractionation even at reduced pressure.

**Operation with Methyl Disulfide, (CH<sub>3</sub>S)<sub>2</sub>.**—Hoffmann and Simmons<sup>3d</sup> have shown that longer chain (*n*- and *t*-butyl disulfides yielded material of the character R<sub>1</sub>SF<sub>3</sub> and (R<sub>1</sub>)<sub>2</sub>SF<sub>4</sub>. However, they used voltages in excess of 5 volts or branched structured starting materials. The possibility that lower voltages or a simpler starting material might result in retention of the chain to form R<sub>1</sub>SF<sub>4</sub>SF<sub>4</sub>R<sub>1</sub> prompted this attempt.

The starting material, b.p. 109–111°, purchased from Eastman Organic Chemicals was used as shipped. Using the same procedures as outlined in the other operations some 282 g. (3.1 moles) of the disulfide was run at 4.5 ± 0.3 volts at an average of 13.1 amp. Enough current was passed to theoretically release 2375 l. of hydrogen gas, but only 634 l. was metered. If the only product were assumed to be CF<sub>3</sub>SF<sub>5</sub>, 3.1 moles of this material would account for 850 l. of hydrogen at room conditions. Accordingly it must be assumed that the current efficiency in this operation was a poor 26.7%.

The Dry Ice condensate amounted to 393 g. No product was retained in the cell. The estimated liquid air condensate was in the order of 360 g.

Only two significant fractions were isolated. The first was CF<sub>3</sub>SF<sub>5</sub> which amounted to 149 g. and the second was a fraction boiling between 28.1–28.7° (flat at 28.3), which had a constant mol. wt. of 146 and a constant f.p. of –18.7 ± 0.3°. No conceivable structure could be assigned to a compound having the above mol. wt. The fraction was examined chromatographically. When the Kel-F ester column was used only one unresolved peak appeared. However, the peak was broad for the b.p. and temp. of operation (30°) and consequently was suspect. When a hexadecane column was used, the chromatogram resolved into two peaks with area ratios in the order of 3:7. An infrared spectrum showed reasonable C–H evidence. Chemically the mixture was unaffected by both concentrated NaOH and H<sub>2</sub>SO<sub>4</sub>. Its proximate density at room temp. was 1.65.

A n.m.r. spectrum of this mixture for fluorine resonance confirmed the presence of both SF<sub>3</sub> and SF<sub>4</sub> groups. A proton resonance spectrum showed both CH<sub>3</sub> and CH<sub>2</sub> assignments. On the basis of the spectral data it was presumed that the mixture contained approximately 70% CH<sub>3</sub>SF<sub>5</sub> and 30% CH<sub>3</sub>SF<sub>4</sub>CH<sub>2</sub>F by wt. These substances have molecular weights of 142 and 157, respectively. If it is assumed that the above noted compounds are the only components present, using the mol. wt. of 146 as a criterion, the exact composition of the mixture would be 73.3% CH<sub>3</sub>SF<sub>5</sub> and 26.7% CH<sub>3</sub>SF<sub>4</sub>CH<sub>2</sub>F and the calculated analysis for such a composition would be S, 21.95; F, 65.05; H, 2.42; C, 10.45. The determined analyses were S, 22.27; F, 65.05; H, 2.25; C, 10.43.

A check of the solubility characteristics of the mixture showed it to be quite soluble in organic solvents such as benzene, MeOH, ether and CCl<sub>4</sub>, but rather immiscible in water, CS<sub>2</sub> and fluorocarbons.

An attempt was made to separate the mixture of CH<sub>3</sub>SF<sub>5</sub> and CH<sub>3</sub>SF<sub>4</sub>CH<sub>2</sub>F chromatographically and determine their properties separately. Unfortunately the material was inadvertently lost.

### Discussion of the Results

In reporting this work the authors are cognizant that, as yet, the electrochemical process of preparing fluorine-containing material in HF is still an art in many respects. The conditions of operation—and there are a multiplicity of operational variables—are based on highly empirical considerations. For example, although the voltage and current density are irrevocably related, it is logically presumed that a low voltage condition favors reduced fragmentation of the original chain of the starting material. At the same time, such a con-

dition could favor incomplete replacement of H or F atoms in the process. Also, as a consequence of the large amount of products that go unidentified, any attempt to suggest a mechanism for what occurs in the cell would be mere conjecture. It can only be stated, with some assurance, that from the nature of the products that are identified, conditions are made available wherein fragmentation, regrouping of the fragments, cyclization and decyclizations of the starting material chain do occur.

The case of *s*-trithiane presents an admirable example of fragmentation, wherein it appears that almost every C–S bond is in some way affected. The appearance of S and CS<sub>2</sub> in the products is enigmatic.

In the case of CH<sub>3</sub>SC<sub>2</sub>H<sub>4</sub>SCH<sub>3</sub>, cyclization appears to occur as evidenced by the formation of (C<sub>2</sub>F<sub>4</sub>SF<sub>4</sub>)<sub>2</sub> and even this cyclic skeleton is further degraded with the loss of an S atom to account for the appearance of C<sub>2</sub>F<sub>6</sub>SF<sub>4</sub>C<sub>2</sub>F<sub>6</sub> in the products. Furthermore the formation of both CF<sub>3</sub>SF<sub>5</sub> and C<sub>2</sub>F<sub>6</sub>SF<sub>4</sub>CF<sub>3</sub> suggests the rupture of a S–C bond to produce these fragments albeit not in equimolar amounts.

Similar types of bond rupture also must occur to account for the products found when thioxane was used. Also, the large amount of material boiling above 85°, which was not identified, implies some regrouping of fragments to form products with more than six atoms, C plus S, in the backbone, despite the presence of H in the structures which would tend to raise the b.p.'s as a consequence of hydrogen bonding.

Finally, in the case of methyl disulfide, the results are particularly enlightening, if the conclusions leading to the postulation of the hybrid mixture, CH<sub>3</sub>SF<sub>5</sub> + CH<sub>3</sub>SF<sub>4</sub>CH<sub>2</sub>F, are correct. It would appear, that in the case of sulfur-bearing starting material, the initial electrochemical attack is on the S atom.

Table I lists the simple properties of all the substances isolated in this work. It will be observed that the SF<sub>4</sub> and/or the SF<sub>5</sub> group in fluorocarbon material has a not inconsiderable contribution to the b.p., *n*<sub>D</sub> and density of the substance in question. Molar refraction calculations of the di- and tri-S-bearing materials were made but are not reported as there was no agreement with the observed values, if current atomic refraction values<sup>3d</sup> are used.

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