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A Plasma Synthesis for the Perfluoroalkyl Di-, Tri-, and Tetrasulfides: Reaction of Trifluoromethyl Radicals with Sulfur Vapor
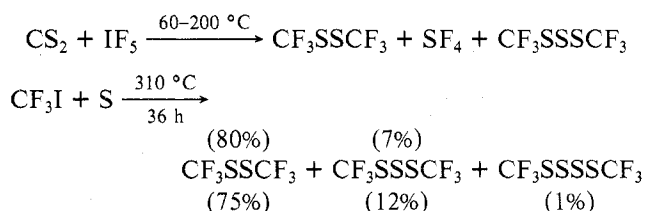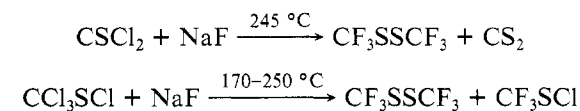
TAKASHI YASUMURA and RICHARD J. LAGOW*[1]

A new synthesis for a number of perfluoroalkyl di-, tri-, and tetrasulfides ($CF_3S_nCF_3$, $C_2F_5S_nCF_3$, $C_2F_5S_nC_2F_5$, $n = 2$–4) has been developed using a low-temperature glow discharge to dissociate sulfur vapor and generate trifluoromethyl radicals from hexafluoroethane. These compounds were characterized by mass spectra, infrared spectra, and NMR spectra.
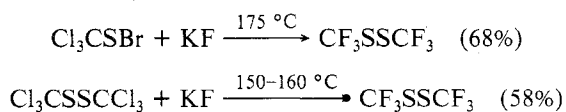
Introduction

Bis(trifluoromethyl) di-, tri-, and tetrasulfides are more stable than their unfluorinated analogues. Previous preparations for these compounds include[2,3]

$$CS_2 + IF_5 \xrightarrow{60\text{–}200\ ^\circ C} CF_3SSCF_3 + SF_4 + CF_3SSSCF_3$$

$$CF_3I + S \xrightarrow[36\ h]{310\ ^\circ C}$$

$$\begin{array}{cc} (80\%) & (7\%) \\ CF_3SSCF_3 + CF_3SSSCF_3 + CF_3SSSSCF_3 \\ (75\%) \quad\quad (12\%) \quad\quad\quad (1\%) \end{array}$$

The most often used preparation for bis(trifluoromethyl) disulfide is the reaction of sodium fluoride with thiocarbonyl chloride or trichloromethanesulfenyl chloride in tetramethylene sulfone solution.[4,5]

$$CSCl_2 + NaF \xrightarrow{245\ ^\circ C} CF_3SSCF_3 + CS_2$$

$$CCl_3SCl + NaF \xrightarrow{170\text{–}250\ ^\circ C} CF_3SSCF_3 + CF_3SCl$$

Other similar procedures are[6]

$$Cl_3CSBr + KF \xrightarrow{175\ ^\circ C} CF_3SSCF_3 \quad (68\%)$$

$$Cl_3CSSCCl_3 + KF \xrightarrow{150\text{–}160\ ^\circ C} CF_3SSCF_3 \quad (58\%)$$

We have previously shown that synthetically useful quantities of reactive trifluoromethyl radicals may be obtained from a glow discharge of hexafluoroethane.[7]

Sulfur vapor (mainly S_8) was introduced into the radiofrequency discharge to be dissociated to generate reactive lower molecular weight species:

$$S_n \text{ (vapor)} \xrightarrow{rf} S + S_2 + S_3 + S_4 + \dots$$
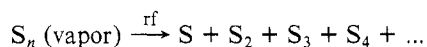
Through the cocondensation of sulfur vapor and reactive plasma-generated trifluoromethyl radicals, a new route to perfluoroalkyl polysulfides was sought.

Experimental Section

Materials. The sulfur was J. T. Baker sublimed sulfur, N. F. The hexafluoroethane used was Matheson high-purity Freon 116.

A Bendix gas chromatograph equipped with a nickel thermal conductivity detector and a cryogenic temperature controller was used for separations. A 7 m by $^3/_8$ in. column of 10% fluorosilicone on Chromosorb P was used.

Physical Measurements. Infrared spectra of gas-phase products were run in a 10-cm cell with KBr windows using a Beckman IR-20A instrument.

Mass spectra were obtained on a Hitachi RMU-6D mass spectrometer at 70 eV. The species containing sulfur were identified by their isotope patterns.

Fluorine NMR spectra were obtained with a Perkin-Elmer R-20B spectrometer operating at a frequency of 56.47 MHz. Chemical shifts were measured with a Takeda-Riken TR-3824X frequency counter.

Analyses were done by Schwarzkopf Microanalytical Laboratories.

Apparatus. The radio-frequency power source was a Tegal Corp. Model RF6100 100-W, 13.56-MHz radio-frequency generator with a matching network operating at approximately 20 W.

The apparatus in which the syntheses were carried out is shown in Figure 1.

Hastings thermocouple vacuum gauges (A), Model DV-5M or Model DV-4DM, were used to monitor the system pressure. A Viton O-ring junction (B) connected the two plates of two Pyrex glass reactors.

The helical coil (C) consists of six turns of $^3/_{16}$-in. copper tubing and is connected to the radio-frequency oscillator.

The C_2F_6 was introduced at the inlet (D) of the reactor. The solid sulfur was heated to the desired temperature using a mantle heater. The two Pyrex traps (E) before the vacuum pump were cooled using liquid nitrogen.

General Procedure. Sulfur powder was placed in the bottom of the reaction chamber. A liquid-nitrogen trap was placed before the pump, and the system was evacuated to less than 5 mTorr.

The sulfur powder was heated to the desired temperature (>165 °C) and C_2F_6 was introduced into the reactor. The system pressure, which was equal to the C_2F_6 pressure (the sulfur vapor condensed rapidly), was measured by a thermocouple vacuum gauge. A Dewar containing liquid nitrogen was put around the product trap. The blue-colored plasma was then initiated.

After the reaction, the system pressure was measured.

Slush baths of various temperatures were used for low-temperature vacuum fractionation. Each product from each fractionation was then examined by IR spectroscopy. Further GC separations were then carried out. The pure products separated by GC were examined by infrared spectroscopy, mass spectroscopy, NMR spectroscopy, and elemental analysis.

Reaction of Sulfur Vapor with Trifluoromethyl Radicals

Sulfur powder was heated to the liquid state at ca. 165 °C. (The temperature was estimated without the plasma under the same conditions as were used during the reaction.) C_2F_6 at a pressure of 100 mTorr was introduced into the reactor from the C_2F_6 inlet tube in front of the radio-frequency coil. After a 6 h run, the contents in the liquid-nitrogen trap were fractionated at –35.6, –78, and –131 °C, and each fraction was further separated by gas chromatography. The –131 °C fraction contained C_2F_6. The –35.6 and –78 °C fractions were separated by GC at a column temperature of 30 °C.
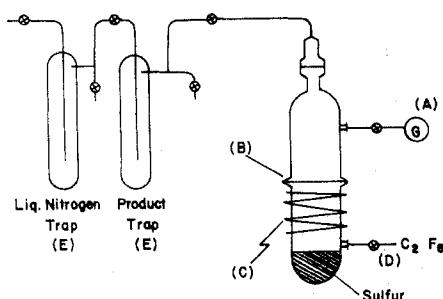
Figure 1. Plasma apparatus.

The colorless products, CF_3SSCF_3, CS_2, $CF_3SSC_2F_5$, $C_2F_5SSC_2F_5$, CF_3SSSCF_3, $CF_3SSSC_2F_5$, $C_2F_5SSSC_2F_5$, $CF_3SSSSCF_3$, and $CF_3SSSSC_2F_5$ (listed in order of GC retention time), were obtained and the weight ratio between CF_3SSCF_3, CS_2, $CF_3SSC_2F_5$, CF_3S-$SSCF_3$, $CF_3SSSC_2F_5$, and $CF_3SSSSCF_3$ were determined to be 32:16:17:3:27:2:3. $C_2F_5SSSC_2F_5$ and $CF_3SSSSC_2F_5$ were minor products and present only in small amounts. About 2 g of the volatile products comprising these fractions were collected in a 4-h period.

Approximately 0.6 g of a yellow rubber-like polymer with a high sulfur content was also obtained from the upper chamber of the reactor.

Bis(trifluoromethyl) Disulfide, CF_3SSCF_3. CF_3SSCF_3 was characterized by its mass spectrum,[8,9] which contained a parent peak at m/e 202, and its infrared spectrum, which agreed exactly with that reported previously by Haszeldine.[2,10] The fluorine NMR spectrum consisted of a single peak at -30.1 ppm from external trifluoroacetic acid (TFA).

Carbon Disulfide, CS_2. Carbon disulfide was identified by means of its IR spectrum and its GC retention time.

Trifluoromethyl Pentafluoroethyl Disulfide, $CF_3SSC_2F_5$. The mass spectrum of $CF_3SSC_2F_5$ contained a parent peak at m/e 252. Other prominent peaks in the spectrum were at m/e 133 ($CF_3S_2^+$), 119 ($C_2F_5^+$), 82 (CF_2S^+), 76 (CS_2^+), 69 (CF_3^+), 64 (S_2^+), 63 (CFS^+), 44 (CS^+), and 32 (S^+).

The fluorine NMR spectrum showed three peaks: -30.2 (triplet, $J = 5.4$ Hz, CF_3SS-), $+6.1$ (triplet ?, $-SSCF_2CF_3$), and $+17.9$ ppm (multiplet, $-SSCF_2CF_3$), from external TFA. The resonances CF_3SS, CF_3CF_2SS-, and CF_3CF_2SS- were integrated and ratios of 3:3:2 were determined, respectively.

The vapor-phase IR absorptions were as follows: 1340 (s), 1230 (vs), 1190 (vs), 1130–1110 (vs, doublet), 950 (s, doublet), 760 (m) cm^{-1}. Anal. Calcd for $CF_3SSC_2F_5$: S, 25.4. Found: S, 25.68.

The fluorine NMR chemical shift of $CF_3SSC_2F_5$ is similar to that of CF_3SSCF_3. CF_3SS- and $-SSCF_2CF_3$ showed long-range coupling between them. The splitting of $SSCF_2CF_3$ was complex.

The IR absorption at 1340 cm^{-1} is probably due to the CF stretching vibration of $-SSCF_2$-. The three strong bands at 1230, 1190, 1130–1110 cm^{-1} can be attributed to a CF$_3$ stretching modes.[11,12]

Bis(pentafluoroethyl) Disulfide, $C_2F_5SSC_2F_5$. The mass spectrum exhibited a parent peak at m/e 302. Other prominent peaks in the spectrum were at m/e 283 ($C_2F_5SSC_2F_4^+$), 183 ($C_2F_5S_2^+$), 119 ($C_2F_5^+$), 82 (CF_2S^+), 69 (CF_3^+), 64 (S_2^+), 63 (CFS^+), 44 (CS^+), and 32 (S^+).

The fluorine NMR spectrum (external TFA reference) showed two peaks, one at 6.3 ppm (CF_3CF_2-) and the other at 18.1 ppm ($-CF_2CF_3$) with an integral ratio of 3:2.

The vapor-phase IR absorptions were 1340 (s), 1235 (vs), 1190 (m), 1130 (m), 955 (s), and 755 (m) cm^{-1}.

Bis(trifluoromethyl) Trisulfide, CF_3SSSCF_3. The mass spectrum contained a parent peak at m/e 234. Other prominent peaks in the spectrum were at m/e 165 ($CF_3S_3^+$), 133 ($CF_3S_2^+$), 82 (CF_2S^+), 69 (CF_3^+), 64 (S_2^+), 63 (CFS^+), 44 (CS^+), and 32 (S^+).
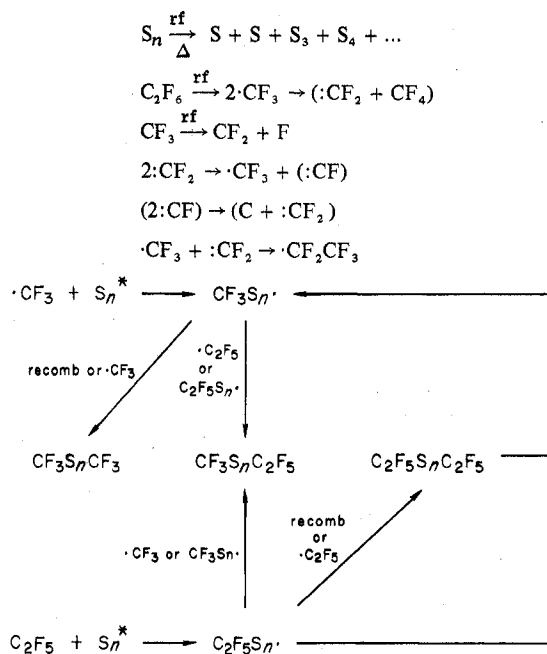
The fluorine NMR spectrum showed a single peak at -30.8 ppm from external TFA.

The vapor-phase IR absorptions were 1180 (vs), 1110 (vs), and 760 (m) cm^{-1}.

The mass spectrum was in agreement with the previously reported spectra for CF_3SSSCF_3.[9,13]

The infrared spectrum agreed also with that previously reported for CF_3SSSCF_3.[2]

Trifluoromethyl Pentafluoroethyl Trisulfide, $CF_3SSSC_2F_5$. The mass spectrum of $CF_3SSSC_2F_5$ contained a parent peak at m/e 284. Other prominent peaks in the spectrum were at m/e 215 ($C_2F_5S_3^+$), 183

Scheme I^a

$$S_n \xrightarrow[\Delta]{rf} S + S + S_3 + S_4 + \ldots$$

$$C_2F_6 \xrightarrow{rf} 2 \cdot CF_3 \rightarrow (:CF_2 + CF_4)$$

$$CF_3 \xrightarrow{rf} CF_2 + F$$

$$2:CF_2 \rightarrow \cdot CF_3 + (:CF)$$

$$(2:CF) \rightarrow (C + :CF_2)$$

$$\cdot CF_3 + :CF_2 \rightarrow \cdot CF_2CF_3$$

^{a} S* indicates sulfur vapor plasma.

($C_2F_5S_2^+$), 165 ($CF_3S_3^+$), 133 ($CF_3S_2^+$), 119 ($C_2F_5^+$), 82 (CF_2S^+), 69 (CF_3^+), 64 (S_2^+), 63 (CFS^+), and 32 (S^+).

The fluorine NMR spectrum consisted of three peaks: -31.2 (triplet, CF_3SSS-), $+5.7$ (triplet, $-SSSCF_2CF_3$), and $+18.3$ ppm (multiplet, $-SSSCF_2CF_3$), from external TFA, with an integral ratio of 3:3:2.

CF_3SSS- and $-SSSCF_2CF_3$ exhibited long-range coupling in the NMR spectrum. CF_3SSS- and $-SSSCF_2CF_3$ clearly showed a triplet signal.

The vapor-phase IR absorptions were 1340 (s), 1230 (vs), 1185 (vs), 1120 (vs), 970 (m), 955 (m), and 760 (m) cm^{-1}.

The infrared spectrum of $CF_3SSSC_2F_5$ was similar to that of $CF_3SSC_2F_5$. Anal. Calcd for $CF_3SSSC_2F_5$: S, 33.8. Found: S, 33.87.

Bis(pentafluoroethyl) Trisulfide, $C_2F_5SSSC_2F_5$. A parent peak at m/e 334 was obtained for $C_2F_5SSSC_2F_5$. Other prominent peaks in the spectrum were at m/e 215 ($C_2F_5S_3^+$), 183 ($C_2F_5S_2^+$), 132 ($C_2F_4S^+$), 119 ($C_2F_5^+$), 82 (CF_2S^+), 76 (CS_2^+), 69 (CF_3^+), 64 (S_2^+), 63 (CFS^+), 44 (CS^+), and 32(S^+).

The vapor-phase IR contained absorptions at 1340 (s), 1240 (vs), 1190 (s), 1125 (vs), 960 (s), and 760 (m) cm^{-1}.

Anal. Calcd for $C_2F_5SSSC_2F_5$: S, 28.7. Found: S, 28.50.

The infrared spectrum of $C_2F_5SSSC_2F_5$ was similar to that of $C_2F_5SSC_2F_5$.

Bis(trifluoromethyl) Tetrasulfide, $CF_3SSSSCF_3$. A parent peak at m/e 266 was seen in the mass spectrum. Other prominent peaks in the spectrum were at m/e 197 ($CF_3S_4^+$), 165 ($CF_3S_3^+$), 133 ($CF_3S_2^+$), 82 (CF_2S^+), 69 (CF_3), 64 (S_2^+), 63 (CFS^+), 44 (CS^+), and 32 (S^+).

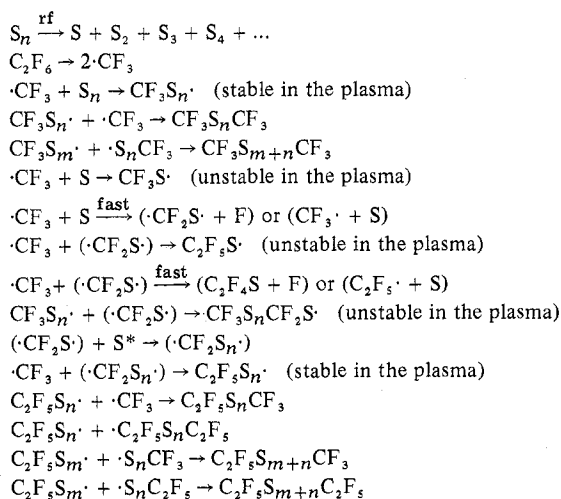The fluorine NMR spectrum consisted of a single peak at -32.6 ppm from external TFA.

The vapor-phase IR absorptions were at 1280 (vs), 1110 (vs), and 760 (m) cm^{-1} in agreement with the previous report of Haszeldine.[2]

Trifluoromethyl Pentafluoroethyl Tetrasulfide, $CF_3SSSSC_2F_5$. A parent peak at m/e 316 was seen in the mass spectrum. Other prominent peaks in the spectrum were at m/e 284 ($C_2F_5S_3CF_3^+$), 265 ($C_3F_7S_3^+$), 234 ($C_2F_6S_3^+$), 215 ($C_2F_5S_3^+$), 197 ($CF_3S_4^+$), 183 ($C_2F_5S_2^+$), 165 ($CF_3S_3^+$), 133 ($CF_3S_2^+$), 119 ($C_2F_5^+$), 82 (CF_2S^+), 69 (CF_3^+), 64 (S_2^+), 63 (CFS^+), 44 (CS^+), and 32 (S^+).

The vapor-phase IR absorptions were at 1330 (s), 1230 (vs), 1180 (vs), 1115 (vs), 965 (s), and 760 (s) cm^{-1}.

Results and Discussion

A possible, and perhaps the most obvious, series of mechanistic steps which are consistent with the observed products are listed in Scheme I. One observation which is quite surprising is that no CF_3SCF_3 is observed in the reaction products. One possible explanation, of course, is that there

Scheme II[a]

$$S_n \xrightarrow{rf} S + S_2 + S_3 + S_4 + \ldots$$

$$C_2F_6 \rightarrow 2 \cdot CF_3$$

$$\cdot CF_3 + S_n \rightarrow CF_3S_n \cdot \quad \text{(stable in the plasma)}$$

$$CF_3S_n \cdot + \cdot CF_3 \rightarrow CF_3S_nCF_3$$

$$CF_3S_m \cdot + \cdot S_nCF_3 \rightarrow CF_3S_{m+n}CF_3$$

$$\cdot CF_3 + S \rightarrow CF_3S \cdot \quad \text{(unstable in the plasma)}$$

$$\cdot CF_3 + S \xrightarrow{fast} (\cdot CF_2S \cdot + F) \text{ or } (CF_3 \cdot + S)$$

$$\cdot CF_3 + (\cdot CF_2S \cdot) \rightarrow C_2F_5S \cdot \quad \text{(unstable in the plasma)}$$

$$\cdot CF_3 + (\cdot CF_2S \cdot) \xrightarrow{fast} (C_2F_4S + F) \text{ or } (C_2F_5 \cdot + S)$$

$$CF_3S_n \cdot + (\cdot CF_2S \cdot) \rightarrow CF_3S_nCF_2S \cdot \quad \text{(unstable in the plasma)}$$

$$(\cdot CF_2S \cdot) + S^* \rightarrow (\cdot CF_2S_n \cdot)$$

$$\cdot CF_3 + (\cdot CF_2S_n \cdot) \rightarrow C_2F_5S_n \cdot \quad \text{(stable in the plasma)}$$

$$C_2F_5S_n \cdot + \cdot CF_3 \rightarrow C_2F_5S_nCF_3$$

$$C_2F_5S_n \cdot + \cdot C_2F_5S_nC_2F_5$$

$$C_2F_5S_m \cdot + \cdot S_nCF_3 \rightarrow C_2F_5S_{m+n}CF_3$$

$$C_2F_5S_m \cdot + \cdot S_nC_2F_5 \rightarrow C_2F_5S_{m+n}C_2F_5$$

[a] S* indicates sulfur vapor plasma. m and $n \geq 2$.

Table I. Fluorine NMR Chemical Shifts of Perfluoroalkyl Polysulfides

	chemical shift,[a] ppm		
	$-CF_3$	$-CF_2CF_3$	$-CF_2CF_3$
CF_3SCF_3	$(-37.9)^b$		
CF_3SSCF_3	-30.1 s		
CF_3SSSCF_3	-30.8 s		
$CF_3SSSSCF_3$	-32.6 s		
$CF_3SSC_2F_5$	-30.2 t	17.9 m	6.1 t?
$CF_3SSSC_2F_5$	-31.2 t	18.3 m	5.7 t
$C_2F_5SSC_2F_5$		18.1	6.3

[a] Chemical shifts are in ppm relative to external TFA. [b] Corrected to reference TFA from the internal $CFCl_3$ reported.[16]

may be a very low percentage of monoatomic sulfur in a relatively low energy (~ 20 W) plasma.

Another rather strange feature of this reaction is the isolation of substantial quatities of the pentafluoroethyl compounds $CF_3S_nC_2F_5$ and $C_2F_5S_nC_2F_5$. This would certainly suggest the generation of C_2F_5 radicals from C_2F_6 under plasma conditions. This might not be surprising to the casual reader. However, significant quantities of $M(C_2F_5)_n$ organometallics have not been observed in the course of our previous work with hexafluoroethane plasmas.[7]

A clue which raises the possibility of an alternate mechanistic process lies in the observation of the mass spectra of perfluoroalkyl polysulfides. Radicals and ions in low-temperature "glow" discharges are formed by collisions of molecules with energetic electrons, and the situation is mechanistically very similar to the generation of ions by electron bombardment in the source of a mass spectrometer. Quite interestingly, the monosulfur perfluoroalkyl ions, such as $(CF_3S)^+$ and $(C_2F_5S)^+$, are not observed in the mass spectrum of perfluoroalkyl polysulfides, while species of the type $CF_3S_n^+$ and $C_2F_5S_n^+$ are peaks of high intensity. Other studies have shown that $(CF_3S)^+$ is a very low intensity feature, while $(CF_2S)^+$ and $(CFS)^+$ are major spectral features.[8,9,13] It is reasonable to suggest, therefore, that CF_3S^+ is a relatively unstable ion and must have a very short half-life as a gas-phase species.

An alternative mechanistic scheme which is consistent with the assumption that $CF_3 \cdot$ and $C_2F_5 \cdot$ are relatively unstable in the plasma and decompose readily is presented in Scheme II.

The fluorine NMR spectra of some perfluoroalkyl polysulfides are summarized in Table I.

The chemical shift differences between the CF_3 groups of the compounds $CF_3S_nCF_3$ ($n \geq 2$) are all very small. It seems reasonable that the chemical shift of $CF_3S_nCF_3$ ($n \geq 2$) decreases as n increases, and the tendency is analogous to the effect Tiers reported for $(n\text{-}C_3F_7)_2S_n$ and the effect Thompson reported for $(CF_3)_2O_n$.[14,15]

Interestingly, $CF_3S_n^-$ and $-S_nCF_2CF_3$ ($n = 2,3$) show long-range coupling and the $CF_3S_n^-$ signal is split into three peaks, but the coupling constant $J(CF_3\text{-}CF_2)$ is very small.

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