Contribution from the Department of Chemistry,
The University of Oklahoma, Norman, Oklahoma 73069

High-Pressure Interaction of Sulfur Hexafluoride with Carbon Disulfide and Carbonyl Sulfide[1]

ARNULF P. HAGEN* and BILL W. CALLAWAY

Received March 27, 1975 AIC502319

Sulfur hexafluoride has been found to react with carbon disulfide and carbonyl sulfide. At a minimum of 485° (1360 atm) with carbon disulfide the products are $(CF_3)_2S$, $(CF_3)_2S_2$, carbon, and sulfur. Carbonyl sulfide reacts at 500° (270 atm) forming CF_4, SOF_2, and sulfur. No reaction takes place with carbon monoxide or carbon dioxide at conditions up to 500° (4000 atm). Graphite reacts at 500° (135 atm) forming CF_4 and SF_4 in a reaction which becomes nearly quantitative at 500° (4000 atm). When $(CF_3)_2S_2$ is combined with carbon disulfide at 540° (4000 atm) the products include carbon, sulfur, and fluoroalkanes. The observed interaction of CO_2, COS, and CS_2 with SF_6 can be best explained by an initial reaction which results in the formation of SF_4, COF_2 or CSF_2, and sulfur.

Few reaction systems which include sulfur hexafluoride have been studied, even though many reactions are thermodynamically possible at standard conditions.[2] At moderate temperatures in a sealed glass ampoule it has been found to react with $AlCl_3$ and SO_3. The former reaction at 200° formed sulfur chlorides and the latter at 250° led to a 20% conversion to form SO_2F_2.[3] In a previous study we have shown SF_6 to react with a series of oxides including MgO, NiO, SiO_2, and water with a 10% conversion of SO_2F_2 at 475° (130 atm) and 90% conversions at 500° (3300–4000 atm).[4]

Results and Discussion

Sulfur hexafluoride has been found to react with carbon disulfide and carbonyl sulfide but not with CO_2 at conditions of temperature and pressure up to 500° (4000 atm). The results are summarized in Table I. The reaction

$$2CS_2(g) + SF_6(g) \rightarrow (CF_3)_2S_2(g) + 3S(s)$$

was observed at 485° (1350 atm) with a 19% conversion of SF_6; when the pressure was increased to 4000 atm, a 73% conversion of SF_6 was obtained, and at 495° (4000 atm) 90% of the SF_6 was consumed. This reaction is analogous to the low-pressure reactions of CS_2 with IF_5 (195°),[5] HgF_2 (460°),[6] and UF_6 (25°),[7] and, in the presence of catalytic amounts of AsF_3 or BF_3, SF_4 (200°).[8] The recovered $(CF_3)_2S$ was formed from the thermal decomposition of $(CF_3)_2S_2$ which has been demonstrated to take place at low[9] and high pressures.

Since in this work CS_2 was found to undergo thermal decomposition at the temperatures and pressures where reaction took place, experiments were designed to determine whether the initial reaction of SF_6 was with carbon disulfide, carbon, or sulfur. Sulfur hexafluoride did not react with carbon at 450° (4000 atm), but at 500° (135 atm) a 20% reaction took place, and at 500° (4000 atm) the reaction

$$2SF_6(g) + C(s) \rightarrow 2SF_4(g) + CF_4(g)$$

was nearly quantitative. At 500° (4000 atm) neither SF_6 nor CF_4 reacted with sulfur and CF_4 did not react with carbon or carbon disulfide. The lack of CF_4 in the reaction between SF_6 and carbon disulfide eliminated the formation of SF_4 by an initial reaction of SF_6 with carbon as the primary reaction.

Above 500° the reaction between carbon disulfide and SF_6 became more complex. In addition to thermal decomposition, the $(CF_3)_2S_2$ reacted with CS_2 or SF_6. At 540° (270 atm) SF_6 and $(CF_3)_2S_2$ did not react, but when the pressure was increased to 4000 atm, CF_4 and SF_4 were formed. At 540° (270 atm) CS_2 and $(CF_3)_2S_2$ interacted forming CF_4, SF_4, and sulfur. When the pressure was increased to 4000 atm several fluoroalkanes up to C_5F_{12} were also isolated.[9]

No reaction was found between SF_6 and carbon dioxide at 500° (4000 atm). This lack of reaction is important in itself. It rules out the thermal decomposition of SF_6 to form SF_4 as the primary reaction since CO_2 and SF_4 have been shown to form COF_2 and CF_4 at high temperatures.[10]

The reactions of SF_6 with carbonyl sulfide were observed at lower pressures than for the reaction of SF_6 with CS_2. The results are summarized in Table II. No reaction took place at 450° (4000 atm) or at 500° (170 atm), but at 500° (270 atm) all of the SF_6 reacted according to the equation

$$COS(g) + SF_6(g) \rightarrow SOF_2(g) + CF_4(g) + S(s)$$

The same stoichiometry was obtained whether the SF_6 or the COS was in excess.

Previous workers have shown that COS decomposed via two independent simultaneous equilibria

$$2COS(g) \rightleftarrows CO_2(g) + CS_2(g)$$

$$COS\ (g) \rightleftarrows CO(g) + S(s)$$

It was noticed that these reactions were sensitive to the vessel used for reaction.[11] For example more decomposition was noted when "Jena" glass vessels were used or silica was placed in a "Pyrex" vessel than was noted for a "clean Pyrex" reaction. In this laboratory no decomposition was noted at 500° and at 170, 270, or 4000 atm in gold tubing. Even though no thermal decomposition of the carbonyl sulfide had been observed in this study, SF_6 was combined with CO at 500° (4000 atm). No reaction took place in this experiment. Combining this experiment with the previously discussed reactions of CS_2 and the lack of reaction of SF_6 with sulfur and CO_2 indicated the primary reaction was with COS and not with its thermal decomposition products.

There are two reaction sequences which can describe the observed stoichiometry. The first sequence is analogous to the reaction of SF_6 with other oxides which lead to the formation of SO_2F_2[4]

$$SF_6(g) + 2COS(g) \rightarrow SO_2F_2(g) + CF_4(g) + CS_2(g)$$

The SO_2F_2 and CS_2 then react to form SOF_2 and sulfur

$$SO_2F_2(g) + CS_2(g) \rightarrow COS(g) + SOF_2(g) + S(s)$$

In a series of experiments with SO_2F_2 the products of the second reaction were found not to include SOF_2 but did include $(CF_3)_2S_x$ (where x = 1, 2, 3) at 500° (4000 atm)

$$3SO_2F_2(g) + 8CS_2(g) \rightarrow 6COS + (CF_3)_2S_2 + 11S(s)$$

It was not possible to adjust the SO_2F_2:CS_2 ratio to eliminate the formation of $(CF_3)_2S_2$. Since this material was not observed in any of the SF_6 experiments it is not unreasonable to rule out the initial formation of SO_2F_2.

The second reaction sequence has as its first step the formation of COF_2 and SF_4

$$SF_6(g) + COS(g) \rightarrow COF_2(g) + SF_4(g)$$

Table I. SF_6 and CS_2 System

Pressure, atm	Temp, °C	Time, hr	Conversion,[a] %	Amt of reactants, mmol		Amt of material out, mmol						
				SF_6	CS_2	SF_6	CS_2	$(CF_3)_2S_2$	$(CF_3)_2S$	CF_4	SF_4	S[b]
4000	280	18		0.65	0.68	0.65	0.68					
4000	430	18		1.26	1.09	1.26	1.09					
335	485	24		0.87	0.72	0.87	0.72					
1000	485	24		0.79	0.75	0.79	0.75					
1350	485	24	19	0.75	0.52	0.69	0.41	0.02	0.04			0.21
4000	485	18	73	0.82	1.80	0.17	0.48	0.52	0.13			2.01
4000	495	18	90	0.67	1.53		0.15	0.22	0.45			2.46
170	500	24		0.87	0.74	0.87	0.74					
270	520	18	100[c]	1.27	1.07		0.33			0.64	1.27	1.27
4000	540	24	100	0.97	0.91	0.06			0.30	0.30	0.61	1.81

[a] Percent of CS_2 consumed. [b] Calculated. [c] Percent of SF_6 consumed.

Table II. SF_6 and COS System

Pressure, atm	Temp, C	Time, hr	Conversion, %	Amt of reactants, mmol		Amt of material out, mmol				
				SF_6	COS	SF_6	COS	CF_4	SOF_2	S[a]
4000	300	24		1.26	1.26	1.26	1.26			
335	450	20		0.91	0.90	0.91	0.90			
4000	450	18		0.91	0.90	0.91	0.90			
170	500	18		1.15	0.95	1.15	0.95			
270	500	18	100[b]	1.17	1.26		0.90	1.17	1.17	1.17
4000	500	24	100[c]	1.60	1.24	0.36		1.24	1.23	1.24

[a] Calculated. [b] Percent of SF_6 consumed. [c] Percent of COS consumed.

This reaction is then followed by

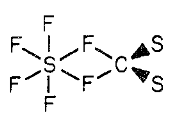
$$SF_4(g) + COF_2(g) \rightarrow SOF_2(g) + CF_4(g)$$

a reaction that has been shown to take place readily without the need for pressure.[10] In related experiments at 500° (4000 atm), CO and COF_2 were found not to be fluorinated by SF_6, and SF_6 was found not to react with sulfur. The reaction

$$SF_6(g) + 5CO(g) + S(s) \rightarrow 3COF_2(g) + 2COS(g)$$

was observed at 500° (4000 atm). In this reaction no CF_4 or SOF_2 was obtained which indicated that the SF_6 and carbonyl sulfide did not react. When COS, SF_6, and COF_2 were combined at 500° (4000 atm), no CF_4 or SOF_2 were obtained and at the same conditions COS and COF_2 did not react.

The reactions of SF_6 with carbon disulfide and carbonyl sulfide are temperature and pressure dependent. These two interactions and the lack of reaction with carbon dioxide can be explained by the initial formation of SF_4 via a coordinated intermediate, $SF_6 \cdot CS_2$



This intermediate then decomposes forming sulfur tetrafluoride

$$SF_6(g) + CS_2(g) \rightarrow CSF_2(g) + SF_4(g)$$

Equations can be written for CS_2, COS, and CO_2 which all involve the same type of coordinated intermediate

$$SF_6(g) + CS_2(g) \rightarrow CSF_2(g) + SF_4(g) + S(s)$$
$$SF_6(g) + COS(g) \rightarrow COF_2(g) + SF_4(g) + S(s)$$
$$SF_6(g) + CO_2(g) \rightarrow COF_2(g) + SF_4(g) + {}^1/_2O_2(g)$$

The different secondary reactions can then be explained by reactions of SF_4 with COF_2 or CS_2 and CSF_2

$$SF_4 + CSF_2 + CS_2 \rightarrow (CF_3)_2S_2 + 2S$$
$$SF_4 + COF_2 \rightarrow CF_4 + SOF_2$$

The lack of any reaction between CO_2 and SF_6 is not surprising since the initial interaction would not be thermodynamically favorable as compared to the COS and CS_2 interactions.

Experimental Section

All experiments were conducted under conditions at which the compounds were relatively thermally stable to minimize extraneous reactions. When an interaction was not observed at or near ambient conditions, the system was then examined at elevated conditions of temperature and pressure.

All work at reduced pressures was carried out in a borosilicate glass vacuum system constructed with Teflon stopcocks (Fischer & Porter Co., Warminster, Pa.). High pressures were generated using a gas pressure booster (High Pressure Equipment Co., Erie, Pa.) attached to a high pressure–high temperature hydrothermal research unit (Model HR-1B-4, Tem-Pres Research, State College, Pa.). The samples were contained in sealed ampoules made from 3-mm diameter thin-walled gold tubing which were placed in a high-pressure reactor. Nitrogen gas was used to generate the desired pressure. At the end of a reaction period the reactor was cooled to −196° before releasing the pressure. The ampoule was removed and placed into an opening device attached to the vacuum line. After warming of the system to room temperature, water, CO_2, and other condensable materials on the surface of the gold tubing were pumped away. The opening device and vacuum line were pretreated with Me_3SiCl or SF_4 to remove any remaining traces of H_2O, and then the ampoule was opened. The substances which volatilized were transferred directly into the vacuum line. Solid material was recovered in a glove bag under an N_2 or Ar atmosphere.

All reaction mixtures were separated by using standard vacuum-line fractionation techniques, except for the removal of SF_4, SOF_2, COF_2, or COS by condensation on powdered moist NaOH. All products were identified and confirmed by two or more techniques including infrared spectroscopy, mass spectroscopy, vapor pressure measurements, melting point determinations, or elemental analysis.

Instrumentation. Infrared absorption spectra were obtained in the 4,000–300 cm^{-1} region using a Beckman Model IR-10 double-beam, grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O rings at reduced pressure. The instrument was calibrated using polystyrene.

The mass spectra were obtained using a Hitachi-Perkin Elmer RMU-7E mass spectrometer with an ionizing potential of 70 eV, current of 50 μA, ion-source temperature of 150°, accelerating potential of 3600 V, and a pressure between 10^{-6} and 5×10^{-5} Torr as measured by the unit's gauge.

Reagents. All reagents were commercial materials. The volatile substances were vacuum distilled just prior to use. Carbon dioxide and COS were purified by distilling the sample through a trap cooled to −95° (toluene slush) to remove impurities of low volatility and then retaining the material which stopped in a trap cooled to −145° (pentane–isopentane slush).[12,13] The same procedure was used to purify $(CF_3)_2S_2$[14] and CS_2[15] using a −78° bath (Dry Ice–acetone mixture) and a −95° bath. Sulfur hexafluoride was purified by the same procedure using a −95 and a −130° (pentane slush) bath.[16] Carbon tetrafluoride was passed through a trap cooled to −130° before use.[17] Sulfur was used as sublimed sulfur flowers. The oxygen-free carbon used in this study was "Sterling MT 2700° Graphitized Carbon" prepared by the Cabot Corp.

Reaction of SF_6 and CS_2. Sulfur hexafluoride (120 mg, 0.823 mmol) and CS_2 (136.8 mg, 1.800 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 485° (4000 atm) for 18 hr. The tube was opened and the volatile material was separated by passing through traps cooled to −95 and −130°. The material that passed was collected at −196°. The −95° trap contained $(CF_3)_2S_2$[14,18] and CS_2 (142.6 mg, 1.006 mmol). The −130° fraction contained $(CF_3)_2S$ (22.4 mg, 0.132 mmol) and the −196° trap held SF_6 (24.1 mg, 0.165 mmol).

Additional experiments are summarized in Table I.

Reaction of SF_6 and CS_2. Sulfur hexafluoride (142 mg, 0.979 mmol) and CS_2 (98.8 mg, 1.30 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 540° (4000 atm) for 24 hr. The tube was opened and the volatile material was condensed at −196°. The mixture was passed through a trap cooled to −130° into a trap at −196°. The former trap contained a mixture of $(CF_3)_2S$[14] and SF_4[19,20] (115 mg, 0.830 mmol) and the −196° trap contained CF_4 (45 mg, 0.42 mmol). The gold tube contained S (84.3 mg, 2.63 mmol).

Reaction of SF_6 and COS. Sulfur hexafluoride (233 mg, 1.60 mmol) and COS (74.4 mg, 1.24 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 500° (4000 atm) for 24 hr. The gold ampoule was opened and the volatile material was condensed at −196°. The volatile material was passed through a trap at −145° into a trap at −196°. The former trap contained a mixture of SF_6 and SOF_2 (159 mg, 1.59 mmol) and the latter CF_4 (109 mg, 1.24 mmol). The gold tube contained S (39.7 mg, 1.24 mmol).

Additional experiments are summarized in Table II.

Reaction of $(CF_3)_2S_2$ and SF_6. Bis(perfluoromethyl) disulfide (162 mg, 0.802 mmol) and SF_6 (206 mg, 1.41 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 540° (4000 atm) for 24 hr. The gold ampoule was opened and the volatile materials were condensed into a trap at −196°. The volatile material was separated by passing through a series of cold traps cooled to −78, −95, −130, −145, and −160° into a trap cooled to −196°. All of the volatile material passed the −78° trap. The material which stopped in the −95° trap was a mixture of CS_2, $(CF_3)_2S_2$, C_5F_{12}, and C_4F_{10}.[21] The −130 and −145° fractions were the same and were combined. This fraction contained C_2F_6 and C_3F_8.[21] The −160° trap contained nothing. The −196° trap contained CF_4 (0.20 mmol). The gold tube contained a mixture of carbon and sulfur.

Reaction of SF_6 with CO and S. Sulfur hexafluoride (127 mg, 0.870 mmol) was condensed into a gold tube which had been charged with sulfur (100 mg, 3.13 mmol) at −196°. Liquid CO was then condensed into the tube at −196° and the tube sealed. The ampoule was held at 500° (4000 atm) for 24 hr and then opened. The material which condensed at −196° was found to be a mixture of SF_6, COS, and COF_2 (177 mg, 2.03 mmol). This mixture after treatment with NaOH yielded only SF_6 (84 mg, 0.58 mmol).

Reaction of SF_6 and Carbon. Sulfur hexafluoride (150 mg, 1.03 mmol) was added to a gold tube which had been charged with carbon (60.1 mg, 5.00 mmol). The tube was sealed and held at 500° (4000 atm) for 24 hr. The ampoule was opened and the volatile materials condensed at −196°. The mixture was passed through a trap cooled to −160° (isopentane slush) into a trap cooled to −196°. The latter trap contained CF_4 (42 mg, 0.48 mmol). The former trap contained SF_4 and a trace of SF_6 (108 mg, 1.00 mmol).

No reaction was found at 450° (4000 atm) and a 20% conversion took place at 500° (135 atm).

Decomposition of CS_2. Carbon disulfide (210.0 mg, 2.763 mmol) was condensed into a gold tube at −196°. The tube was sealed and held at 500° (4000 atm) for 24 hr. The tube was opened and the volatile material was condensed at −196°. The trap contained only CS_2 (125.9 mg, 1.656 mmol). The gold tube contained a mixture of carbon and sulfur. No decomposition was found at 250° (4000 atm) and 51% decomposition was observed at 500° (275 atm).

Reaction of SF_2O_2 and CS_2. In a qualitative experiment sulfuryl fluoride (125.6 mg, 1.231 mmol) and CS_2 (84.06 mg, 1.106 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 395° (4300 atm) for 18 hr. The tube was opened and the volatile material was separated by passing the mixture through a trap cooled to −130° into a trap at −196°. The former trap contained unreacted CS_2 and $(CF_3)_2S_x$ (where $x = 1, 2, 3$; confirmed by mass spectroscopy) and the −196° trap contained SO_2F_2 and COS.

Additional qualitative experiments at 500° (3000 and 4000 atm) gave the same results.

Acknowledgment. The authors wish to thank Dr. H. W. Beck for his assistance in obtaining mass spectral data. This research was supported by National Science Foundation Grant GP-19873.

Registry No. SF_6, 2551-62-4; CS_2, 75-15-0; COS, 463-58-1.

References and Notes

(1) This report is based on portions of a dissertation submitted by B. W. Callaway to The University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(2) M. Kh. Karapet'yants and M. L. Karapet'yants, "Thermodynamic Constants of Inorganic and Organic Compounds", J. Schmorak, Translator, Ann Arbor-Humphrey Science Publishers, Ann Arbor, Mich., 1970.
(3) J. R. Case and F. Nyman, *Nature (London)*, **193**, 473 (1962).
(4) A. P. Hagen, D. J. Jones, and S. R. Ruttman, *J. Inorg. Nucl. Chem.*, **36**, 1217 (1974).
(5) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).
(6) E. H. Man, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 3575 (1959).
(7) L. E. Trevorrow, J. Fischer, and W. H. Gunther, *Inorg. Chem.*, **2**, 1281 (1963).
(8) R. J. Harder and W. C. Smith, *J. Am. Chem. Soc.*, **83**, 3422 (1961).
(9) E. W. Lawless and L. D. Harman, *J. Inorg. Nucl. Chem.*, **31**, 1541 (1969).
(10) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).
(11) J. R. Partington and H. H. Neville, *J. Chem. Soc.*, 1230 (1951).
(12) R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956).
(13) H. J. Collomon, D. C. McKean, and H. W. Thompson, *Proc. R. Soc. London, Ser. A.*, **208**, 341 (1951).
(14) G. R. A. Brandt, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 2549 (1952).
(15) T. Wentink, Jr., *J. Chem. Phys.*, **29**, 188 (1958).
(16) R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, **19**, 534 (1951).
(17) J. Goubeau, W. Bues, and F. W. Kampmann, *Z. Anorg. Allg. Chem.*, **283**, 123 (1956).
(18) H. A. Carter, C. S-C. Wang, and J. M. Shreeve, *Spectrochim. Acta, Part A*, **29**, 1479 (1973).
(19) J. K. O'Loane and M. K. Wilson, *J. Chem. Phys.*, **23**, 1313 (1955).
(20) R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).
(21) American Petroleum Institute Research Project 44, Spectra 196, 401, 444, 445, 729.