

High-Pressure Interaction of Sulfur Hexafluoride with Carbon Disulfide and Carbonyl Sulfide¹

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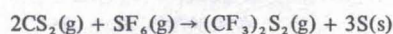
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Sulfur hexafluoride has been found to react with carbon disulfide and carbonyl sulfide. At a minimum of 485° (1360 atm) with carbon disulfide the products are (CF₃)₂S, (CF₃)₂S₂, carbon, and sulfur. Carbonyl sulfide reacts at 500° (270 atm) forming CF₄, SOF₂, 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 CF₄ and SF₄ in a reaction which becomes nearly quantitative at 500° (4000 atm). When (CF₃)₂S₂ is combined with carbon disulfide at 540° (4000 atm) the products include carbon, sulfur, and fluoroalkanes. The observed interaction of CO₂, COS, and CS₂ with SF₆ can be best explained by an initial reaction which results in the formation of SF₄, COF₂ or CSF₂, 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 AlCl₃ and SO₃. The former reaction at 200° formed sulfur chlorides and the latter at 250° led to a 20% conversion to form SO₂F₂.³ In a previous study we have shown SF₆ to react with a series of oxides including MgO, NiO, SiO₂, and water with a 10% conversion of SO₂F₂ at 475° (130 atm) and 90% conversions at 500° (3300–4000 atm).⁴

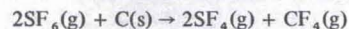
Results and Discussion

Sulfur hexafluoride has been found to react with carbon disulfide and carbonyl sulfide but not with CO₂ at conditions of temperature and pressure up to 500° (4000 atm). The results are summarized in Table I. The reaction



was observed at 485° (1350 atm) with a 19% conversion of SF₆; when the pressure was increased to 4000 atm, a 73% conversion of SF₆ was obtained, and at 495° (4000 atm) 90% of the SF₆ was consumed. This reaction is analogous to the low-pressure reactions of CS₂ with IF₅ (195°),⁵ HgF₂ (460°),⁶ and UF₆ (25°),⁷ and, in the presence of catalytic amounts of AsF₃ or BF₃, SF₄ (200°).⁸ The recovered (CF₃)₂S was formed from the thermal decomposition of (CF₃)₂S₂ which has been demonstrated to take place at low⁹ and high pressures.

Since in this work CS₂ 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 SF₆ 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



was nearly quantitative. At 500° (4000 atm) neither SF₆ nor CF₄ reacted with sulfur and CF₄ did not react with carbon or carbon disulfide. The lack of CF₄ in the reaction between SF₆ and carbon disulfide eliminated the formation of SF₄ by an initial reaction of SF₆ with carbon as the primary reaction.

Above 500° the reaction between carbon disulfide and SF₆ became more complex. In addition to thermal decomposition, the (CF₃)₂S₂ reacted with CS₂ or SF₆. At 540° (270 atm) SF₆ and (CF₃)₂S₂ did not react, but when the pressure was increased to 4000 atm, CF₄ and SF₄ were formed. At 540° (270 atm) CS₂ and (CF₃)₂S₂ interacted forming CF₄, SF₄, and sulfur. When the pressure was increased to 4000 atm several fluoroalkanes up to C₅F₁₂ were also isolated.⁹

No reaction was found between SF₆ and carbon dioxide at 500° (4000 atm). This lack of reaction is important in itself. It rules out the thermal decomposition of SF₆ to form SF₄ as

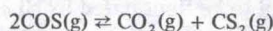
the primary reaction since CO₂ and SF₄ have been shown to form COF₂ and CF₄ at high temperatures.¹⁰

The reactions of SF₆ with carbonyl sulfide were observed at lower pressures than for the reaction of SF₆ with CS₂. 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 SF₆ reacted according to the equation



The same stoichiometry was obtained whether the SF₆ or the COS was in excess.

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

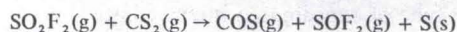


It was noticed that these reactions were sensitive to the vessel used for reaction.¹¹ For example more decomposition was noted when "Jena" glass vessels were used or silica was placed in a "Pyrex" vessel than was noted for a "clean Pyrex" reaction. In this laboratory no decomposition was noted at 500° 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, SF₆ was combined with CO at 500° (4000 atm). No reaction took place in this experiment. Combining this experiment with the previously discussed reactions of CS₂ and the lack of reaction of SF₆ with sulfur and CO₂ indicated the primary reaction was with COS and not with its thermal decomposition products.

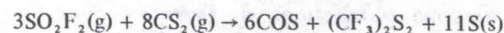
There are two reaction sequences which can describe the observed stoichiometry. The first sequence is analogous to the reaction of SF₆ with other oxides which lead to the formation of SO₂F₂⁴



The SO₂F₂ and CS₂ then react to form SOF₂ and sulfur



In a series of experiments with SO₂F₂ the products of the second reaction were found not to include SOF₂ but did include (CF₃)₂S_x (where x = 1, 2, 3) at 500° (4000 atm)



It was not possible to adjust the SO₂F₂:CS₂ ratio to eliminate the formation of (CF₃)₂S₂. Since this material was not observed in any of the SF₆ experiments it is not unreasonable to rule out the initial formation of SO₂F₂.

The second reaction sequence has as its first step the formation of COF₂ and SF₄

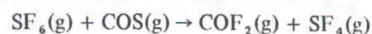


Table I. SF₆ and CS₂ System

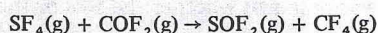
Pressure, atm	Temp, °C	Time, hr	Conversion, % ^a	Amt of reactants, mmol		Amt of material out, mmol						
				SF ₆	CS ₂	SF ₆	CS ₂	(CF ₃) ₂ S ₂	(CF ₃) ₂ S	CF ₄	SF ₄	S ^b
4000	280	18		0.65	0.68	0.65	0.68					
4000	430	18		1.26	1.09	1.26	1.09					
335	485	24		0.87	0.72	0.87	0.72					
1000	485	24		0.79	0.75	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 CS₂ consumed. ^b Calculated. ^c Percent of SF₆ consumed.Table II. SF₆ and COS System

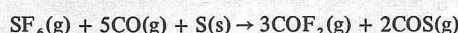
Pressure, atm	Temp, C	Time, hr	Conversion, %	Amt of reactants, mmol		Amt of material out, mmol				
				SF ₆	COS	SF ₆	COS	CF ₄	SOF ₂	S ^a
4000	300	24		1.26	1.26	1.26	1.26			
335	450	20		0.91	0.90	0.91	0.90			
4000	450	18		0.91	0.90	0.91	0.90			
170	500	18		1.15	0.95	1.15	0.95			
270	500	18	100 ^b	1.17	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 SF₆ consumed. ^c Percent of COS consumed.

This reaction is then followed by

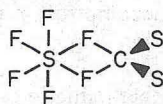


a reaction that has been shown to take place readily without the need for pressure.¹⁰ In related experiments at 500° (4000 atm), CO and COF₂ were found not to be fluorinated by SF₆, and SF₆ was found not to react with sulfur. The reaction

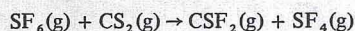


was observed at 500° (4000 atm). In this reaction no CF₄ or SOF₂ was obtained which indicated that the SF₆ and carbonyl sulfide did not react. When COS, SF₆, and COF₂ were combined at 500° (4000 atm), no CF₄ or SOF₂ were obtained and at the same conditions COS and COF₂ did not react.

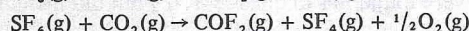
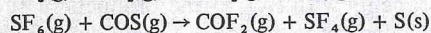
The reactions of SF₆ with carbon disulfide and carbonyl sulfide are temperature and pressure dependent. These two interactions and the lack of reaction with carbon dioxide can be explained by the initial formation of SF₄ via a coordinated intermediate, SF₆-CS₂



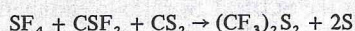
This intermediate then decomposes forming sulfur tetrafluoride



Equations can be written for CS₂, COS, and CO₂ which all involve the same type of coordinated intermediate



The different secondary reactions can then be explained by reactions of SF₄ with COF₂ or CS₂ and CSF₂



The lack of any reaction between CO₂ and SF₆ is not surprising since the initial interaction would not be thermodynamically favorable as compared to the COS and CS₂ 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, CO₂, and other condensable materials on the surface of the gold tubing were pumped away. The opening device and vacuum line were pretreated with Me₃SiCl or SF₄ to remove any remaining traces of H₂O, 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 N₂ or Ar atmosphere.

All reaction mixtures were separated by using standard vacuum-line fractionation techniques, except for the removal of SF₄, SOF₂, COF₂, 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 $(\text{CF}_3)_2\text{S}_2^{14}$ 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 $(\text{CF}_3)_2\text{S}_2^{14,18}$ and CS_2 (142.6 mg, 1.006 mmol). The -130° fraction contained $(\text{CF}_3)_2\text{S}$ (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 $(\text{CF}_3)_2\text{S}^{14}$ and $\text{SF}_4^{19,20}$ (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 $(\text{CF}_3)_2\text{S}_2$ 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 , $(\text{CF}_3)_2\text{S}_2$, 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 sulfonyl 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 $(\text{CF}_3)_2\text{S}_x$ (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.

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

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