

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM &amp; HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

Sulfur Oxyfluoride Derivatives.<sup>1</sup> I

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A simple preparation of SF<sub>2</sub>OF in high yield was developed, and some of its reactions were studied. The reaction of cesium fluoride with several sulfuranyl derivatives was also investigated.

Three sulfur hypofluorite derivatives are known: FSO<sub>2</sub>OF,<sup>2</sup> SF<sub>5</sub>OF,<sup>3</sup> and FSO<sub>2</sub>OOF.<sup>4</sup> Two of these, fluorine fluorosulfonate (FSO<sub>2</sub>OF) and pentafluoro-sulfur hypofluorite (SF<sub>5</sub>OF), were first prepared by a catalytic fluorination procedure in a flow system. It was later shown by Dudley that fluorine fluorosulfonate could be prepared by the action of fluorine on sodium, copper, or nickel fluorosulfonate at 200°, and he proposed that the active intermediates in the catalytic fluorination reactions were the salts AgOSF<sub>5</sub> and Ag-SO<sub>3</sub>F. Since a material having the composition CsOSF<sub>5</sub> was recently reported,<sup>5</sup> a study of the fluorination of thionyl fluoride and thionyl tetrafluoride in the presence of cesium fluoride was undertaken. The action of cesium fluoride on several other sulfur oxyfluoride derivatives was also investigated.

## Experimental

**Materials.**—Cesium fluoride was obtained from Penn Rare Metals, Inc., and was dried at 150° under high vacuum before use. Thionyl fluoride,<sup>7</sup> thionyl tetrafluoride,<sup>8</sup> pyrosulfuryl fluoride,<sup>9</sup> fluorine fluorosulfonate,<sup>2</sup> peroxydisulfuryl difluoride,<sup>9</sup> and cesium fluorosulfonate<sup>10</sup> were prepared by literature methods. Fluorine was obtained from General Chemical Company and was passed through two hydrogen fluoride scrubbers before use. Samples of fluorine were checked periodically by mass spectral analysis to determine the amount of oxygen and oxygen difluoride present.

Pentafluorosulfur fluorosulfonate, SF<sub>5</sub>OSO<sub>2</sub>F, was prepared by a modification of the method of Pass and Roberts.<sup>11</sup> An equimolar gaseous mixture of pentafluorosulfur hypofluorite and sulfur dioxide was irradiated with a G.E. AH4 floodlamp for 4 hr. in a Pyrex bulb. The crude product was obtained by fractionation through a -95° trap and was purified by vapor phase chromatography. The yield was about 30%.

**Analyses of Products.**—Analysis of the volatile products in all of the experiments was performed in a similar manner. Identification of individual species was accomplished by mass and infrared spectroscopy using a Consolidated Engineering Corporation Model 21-620 mass spectrometer. Mass spectrometry was also used for the semiquantitative determination of the relative

amounts of the volatile components in a reaction mixture. Samples of all the products and starting materials involved were purified by vapor phase chromatography or vacuum line fractionation, and their purity was checked by a vapor density determination. These samples were then used to calibrate the mass spectrometer by obtaining the cracking pattern and sensitivity of each material. The relative error in determining the amount of the materials present was no greater than ±2% with two exceptions. Consistent cracking patterns of fluorine fluorosulfonate and peroxydisulfuryl difluoride were difficult to obtain so they could not be estimated accurately.

Complete analysis of the salt residue left in a reaction was not accomplished. The presence of cesium fluorosulfonate, in those reactions where its formation was postulated, was confirmed by infrared analysis<sup>12</sup> when the only other salt present was either potassium fluoride or cesium fluoride. In the reactions where the formation of CsOSF<sub>5</sub> was indicated, the nonvolatile residue was allowed to react with fluorine as described in the next section. The amount of pentafluorosulfur hypofluorite obtained was used as an indication for the extent of formation of CsOSF<sub>5</sub>. In one case SO<sub>2</sub>F<sub>2</sub> was also obtained because excess CsSO<sub>2</sub>F was present.

Table I presents a summary of all of the reactions described. The product compositions listed represent crude reaction mixtures with the exception that the excess fluorine, when present, was first removed.

**Fluorination Study.**—The general procedure used in the fluorination study is described below for one case. Dried cesium fluoride, 10 g., was loaded into a 150-ml. Monel Hoke cylinder, equipped with a Teflon-packed needle valve, in a drybox. The cylinder was prefluorinated at 175° for 12 hr. with an atmosphere of fluorine several times before use. Thionyl fluoride, 3.25 mmoles, was condensed into the cylinder at -196°, and fluorine, 6.82 mmoles, was expanded into the cold cylinder. The amount of fluorine added was calculated from the drop in fluorine pressure in a large calibrated volume. The total fluorine pressure was never allowed to exceed 400 mm. in order to avoid forming a liquid phase. The cylinder was allowed to warm to ambient temperature and stand for 4 hr. After cooling the bomb to -196° any excess fluorine was pumped off through a -196° trap and two soda lime traps. The amount of condensables in the cylinder was determined in a calibrated volume system and then analyzed as described above. Pentafluorosulfur hypofluorite, 3.10 mmoles, and sulfur hexafluoride, 0.10 mmole, were obtained. Traces of sulfuranyl fluoride were also found.

**Preparation of CsSO<sub>2</sub>F, CsSO<sub>3</sub>F, and CsOSF<sub>5</sub>.**—The substrates were prepared in Monel Hoke cylinders by addition of the desired amount of sulfur dioxide, sulfur trioxide, or thionyl tetrafluoride to a weighed amount of cesium fluoride. Excess sulfur dioxide was used while a 1:1 ratio of cesium fluoride to sulfur trioxide was employed. The latter system was heated to 100° for several hours and the first was allowed to stand overnight at 25°. Consumption of the sulfur trioxide was practically complete. Approximately 3 to 5 mmoles of thionyl tetrafluoride and 5 g. of cesium fluoride were heated together at 100° for 1 hr. in a 150-ml. Monel Hoke cylinder. All of the thionyl tetrafluoride was consumed.

(1) This work was performed under Contract No. DA-01-021 ORD-11878.

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TABLE I  
 SUMMARY OF REACTIONS

Substrate <sup>a</sup>	Reactant <sup>a</sup>	Temp. (time)	Products <sup>a</sup>
SOF <sub>2</sub> (3.25) CsF (excess)	F <sub>2</sub> (6.82)	25° (4 hr.)	SF <sub>5</sub> OF (3.10), SF <sub>6</sub> (0.10)
SOF <sub>2</sub> (1.75)	F <sub>2</sub> (3.82)	25° (24 hr.)	SF <sub>4</sub> O (1.53), SO <sub>2</sub> F <sub>2</sub> (0.07), SOF <sub>2</sub> (0.11)
SF <sub>4</sub> O (3.92) CsF (excess)	F <sub>2</sub> (4.04)	25° (4 hr.)	SF <sub>5</sub> OF (3.72), SF <sub>6</sub> (0.13)
SOF <sub>2</sub> (3.34) CsF (excess)	F <sub>2</sub> (3.43)	25° (4 hr.)	SF <sub>5</sub> OF (1.53), SOF <sub>2</sub> (1.48), SF <sub>4</sub> O (0.19), SF <sub>6</sub> (0.05)
CsOSF <sub>5</sub> (1.72) CsF (excess)	F <sub>2</sub> (2.01)	25° (4 hr.)	SF <sub>5</sub> OF (1.63), SF <sub>6</sub> (0.09)
CsOSF <sub>5</sub> (5.12) CsF (excess)	FSO <sub>3</sub> F (1.11)	100° (1 hr.)	SF <sub>5</sub> OF (0.11)} reaction with CsOSF <sub>5</sub> SO <sub>2</sub> F <sub>2</sub> (0.53), O <sub>2</sub> (0.03), OF <sub>2</sub> (0.44)} reaction with CsF
CsSO <sub>2</sub> F (5.27)	FSO <sub>3</sub> F (1.87)	25° (2 hr.)	FSO <sub>2</sub> F (1.78)
CsSO <sub>2</sub> F (3.06)	SF <sub>5</sub> OF (2.17)	100° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (1.98), SF <sub>5</sub> OF <sup>b</sup> (1.77), SO <sub>2</sub> F <sub>2</sub> (1.06) <sup>b</sup>
CsF (excess)	FSO <sub>3</sub> F (7.13)	75° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (3.52), O <sub>2</sub> (0.32), OF <sub>2</sub> (2.91)
KF (excess)	FSO <sub>3</sub> F (3.01)	125° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (1.52), OF <sub>2</sub> (0.86), O <sub>2</sub> (0.29)
CsSO <sub>3</sub> F (excess)	F <sub>2</sub> (6.25)	150° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (1.74), trace O <sub>2</sub> , OF <sub>2</sub> (1.71), unre- acted F <sub>2</sub> not measd.
KSO <sub>3</sub> F (excess)	F <sub>2</sub> (6.20)	150° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (6.21), all F <sub>2</sub> consumed, O <sub>2</sub> (3.18), OF <sub>2</sub> trace
CsF (excess)	S <sub>2</sub> O <sub>6</sub> F <sub>2</sub> (1.78)	75° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (1.74), O <sub>2</sub> (0.83)
CsF (excess)	S <sub>2</sub> O <sub>6</sub> F <sub>2</sub> (4.13)	50° (2 hr.)	SO <sub>2</sub> F <sub>2</sub> (3.72), S <sub>2</sub> O <sub>6</sub> F <sub>2</sub> (0.28)
CsF (excess)	SF <sub>5</sub> OSO <sub>2</sub> F (1.58)	100° (1 hr.)	SO <sub>2</sub> F <sub>2</sub> (1.55), SF <sub>6</sub> trace, SF <sub>5</sub> OF <sup>b</sup> (1.19)

<sup>a</sup> The numbers in parentheses are millimoles of reactants and products. <sup>b</sup> Product obtained upon fluorination of the residue from the reaction.

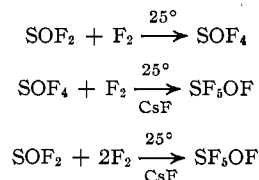
**Reaction of FSO<sub>3</sub>F, SF<sub>5</sub>OF, and Fluorine with the Sulfur Oxyfluoride Anions.**—The same procedure was used in these experiments. It is given below. A 2.17-mmmole sample of pentafluorosulfur hypofluorite was condensed into the cylinder containing 3.06 mmmoles of CsSO<sub>2</sub>F. (When fluorine was used it was simply expanded into the bomb to a known pressure.) The cylinder was allowed to warm and then it was heated to 100° for 1 hr. The amount of volatile components was then determined by expanding them into a calibrated bulb equipped with a manometer. Sulfuryl fluoride, 1.98 mmmoles, was obtained. In order to analyze the solid residue 3.52 mmmoles of fluorine was expanded into the cylinder and the system was allowed to stand for 4 hr. The work-up of the mixture is described above. Pentafluorosulfur hypofluorite, 1.77 mmmoles, and sulfuryl fluoride, 1.06 mmmoles, were obtained. The latter presumably arose from the reaction of fluorine with the excess CsSO<sub>2</sub>F.

**Reactions of Cesium Fluoride with Sulfuryl Derivatives.**—All reactions were conducted in a similar manner. A typical example is: fluorine fluorosulfonate, 7.13 mmmoles, was condensed into a 150-ml. Monel Hoke cylinder containing excess cesium fluoride. The cylinder was heated at 75° for 1 hr. and then cooled to ambient temperature. The total reaction mixture was expanded into a calibrated system with a manometer and the total amount of volatile components determined. A mass spectrum sample was taken from the total mixture for analysis and the infrared showed the absence of any fluorine fluorosulfonate. The following products were found: SO<sub>2</sub>F<sub>2</sub>, 3.52 mmmoles; OF<sub>2</sub>, 2.91 mmmoles; and oxygen, 0.32 mmmoles.

## Results and Discussion

The reaction of fluorine with thionyl fluoride proceeded readily at ambient temperature in a static system. If cesium fluoride were present, then pentafluoro-

sulfur hypofluorite could be consistently isolated in yields greater than 95%. When, however, the cesium fluoride was omitted only thionyl tetrafluoride was found, although an excess of fluorine was used. The conversion of thionyl tetrafluoride to pentafluorosulfur hypofluorite was also easily achieved in the presence of cesium fluoride.



The results suggest a stepwise fluorination of thionyl fluoride to the hypofluorite derivative under the conditions employed. The first step, the formation of thionyl tetrafluoride, does not apparently require a catalyst, whereas further fluorination does.<sup>13</sup> When the fluorination of thionyl fluoride in the presence of cesium fluoride was attempted with equimolar amounts of reagents, the reaction mixture consisted primarily of pentafluorosulfur hypofluorite and unreacted thionyl fluoride. Only a small amount of thionyl tetrafluoride was present in the mixture. It is apparent that the conversion of thionyl tetrafluoride to pentafluorosulfur

(13) The uncatalyzed reaction of fluorine and thionyl fluoride was performed in a prefluorinated Monel cylinder, and some metal fluorides were undoubtedly present. Whether or not they participated in the reaction is unknown.

hypofluorite is faster than the fluorination of thionyl fluoride.

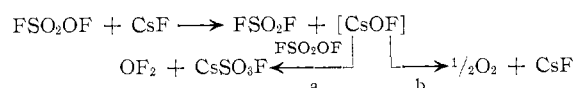
The role of the catalyst in the fluorination of thionyl tetrafluoride is not certain. If an ionic intermediate such as  $\text{CsOSF}_5$  is involved, then fluorination of this salt under the same conditions should occur. Therefore the reaction of thionyl tetrafluoride and cesium fluoride was attempted in an effort to prepare this material. Little or no uptake of the thionyl tetrafluoride by cesium fluoride was observed at ambient temperature. However, at  $100^\circ$  the consumption of thionyl tetrafluoride was rapid, although a complete conversion of the cesium fluoride was not achieved. In the work to be discussed, mixtures of  $\text{CsF}$  and what was presumed to be  $\text{CsOSF}_5$  were employed. Such a mixture was treated with a slight excess of fluorine at ambient temperature and a 95% yield (based on the thionyl tetrafluoride taken up by the  $\text{CsF}$ ) of pentafluorosulfur hypofluorite was obtained. Thus  $\text{CsOSF}_5$  is acceptable as an intermediate. However, under the conditions used in the fluorination of thionyl fluoride it is unlikely that a large amount of this salt is present at one time since little interaction of thionyl tetrafluoride and  $\text{CsF}$  was noted at  $25^\circ$ . The presence of cesium fluoride apparently has an effect on the rate of conversion of thionyl fluoride to thionyl tetrafluoride since the formation of pentafluorosulfur hypofluorite requires much less time than the above uncatalyzed conversion. Therefore, the presence of intermediates such as  $\text{CsOSF}_3$  cannot be eliminated, and an alternate reaction path involving the direct fluorination of  $\text{CsOSF}_3$  to  $\text{CsOSF}_5$  may be possible.

A variation in the catalytic activity of different samples of cesium fluoride was observed. However, an active catalyst could be obtained by heating cesium fluoride to  $100^\circ$  in the presence of thionyl tetrafluoride. After fluorination of the  $\text{CsOSF}_5$  salt thus formed, the residue was sufficiently active to permit clean conversions of thionyl fluoride to pentafluorosulfur hypofluorite under the conditions described in Table I. Sodium fluoride could be employed instead of cesium fluoride but it was less active as a catalyst.

Attempts to oxidize the  $\text{SF}_5\text{O}^-$  anion with either chlorine or pentafluorosulfur hypofluorite were unsuccessful at temperatures up to  $150^\circ$ . Fluorine fluorosulfonate, however, was found to fluorinate the anion to pentafluorosulfur hypofluorite at  $100^\circ$  and no evidence for the mixed peroxide  $\text{FSO}_2\text{OOSF}_5$  was observed. This reaction is in direct contrast to that reported between fluorine fluorosulfonate and nickel fluorosulfonate at  $200^\circ$ , which produces peroxydisulfuryl difluoride.<sup>5</sup> Similar results were obtained when either fluorine fluorosulfonate or pentafluorosulfur hypofluorite was allowed to react with cesium fluorosulfinate. Fluorination of the fluorosulfinate anion to sulfuryl fluoride was observed, and the formation of pyrosulfuryl fluoride or  $\text{SF}_5\text{OSO}_2\text{F}$  was not detected. Elemental fluorine was also found to fluorinate the fluorosulfinate anion in a static system at ambient temperature to sulfuryl fluoride. These results are in agreement with those of

Seel,<sup>10</sup> who reported the same reaction using a flow system.

When fluorine fluorosulfonate was allowed to react with the  $\text{SF}_5\text{O}^-$  anion another reaction in addition to the one discussed above was observed. This second reaction was due to the cesium fluoride present. At  $75^\circ$  fluorine fluorosulfonate and cesium fluoride produced sulfuryl fluoride and oxygen difluoride. A small amount of oxygen was also obtained. It is probable that reaction occurred by a nucleophilic attack of the fluoride ion on the fluorosulfonate group. A reaction which is perhaps formally analogous is the conversion of a  $-\text{CF}_2\text{OSO}_2\text{F}$  fragment to a  $-\text{C}(=\text{O})\text{F}$  group and sulfuryl fluoride by the action of alkali metal fluorides.<sup>14</sup> Two possible sites for nucleophilic attack in fluorine fluorosulfonate are sulfur and the oxygen in the hypofluorite group. The latter possibility is felt to be much less likely than the former, since no reaction was observed between pentafluorosulfur hypofluorite and cesium fluoride at  $150^\circ$ . The oxygen of the hypofluorite group in both of these derivatives should be similar in reactivity toward nucleophiles, whereas the sulfur in the sulfuryl derivative has empty orbitals available and the sulfur in pentafluorosulfur hypofluorite is saturated. Attack of fluoride ion on sulfur would result in the formation of sulfuryl fluoride and an  $\text{OF}^-$  ion. Decomposition of this ion is believed to occur in two ways; fluorination by fluorine fluorosulfonate to oxygen difluoride and thermal decomposition to oxygen and fluoride ion. Thus the reaction scheme is

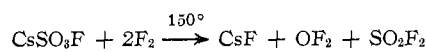


It should be noted that the amount of sulfuryl fluoride obtained is equal to the amount of oxygen difluoride plus twice the amount of oxygen found (see Table I). The same reaction could be accomplished with potassium fluoride except that a temperature of  $125^\circ$  was needed. The higher temperature required probably reflects a lowering of the nucleophilicity of the fluoride ion, as would be expected in going from cesium fluoride to potassium fluoride. Also more oxygen relative to the amount of oxygen difluoride was found when potassium fluoride was employed, although the above stoichiometry was still followed. This suggests more decomposition of the intermediate hypofluorite salt by route b, possibly because of the higher temperature employed or the lower stability of the salt due to a smaller cation.<sup>15</sup> The presence of cesium fluorosulfonate in the salt residue was confirmed by infrared analysis.

The fluorination of cesium or potassium fluorosulfonate in a static system failed to produce any fluorine fluorosulfonate in contrast to the results reported for the fluorination of the sodium salt.<sup>5</sup> Sulfuryl fluoride and either oxygen difluoride or oxygen were obtained depending on which salt was employed.

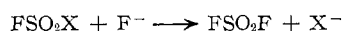
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(15) C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 337 (1964), and references therein.

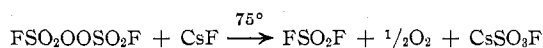


If fluorine fluorosulfonate were formed (as found by Dudley), then under these experimental conditions it would react with the alkali metal fluoride as described above. The lack of oxygen difluoride formation when potassium fluorosulfonate was used is perhaps a result of the increased temperature. The fluorination of sodium fluorosulfonate was performed in a flow system.<sup>5</sup> Thus removal of the fluorine fluorosulfonate could occur before complete reaction with the sodium fluoride was possible.

Cesium fluoride was found to attack several other fluorosulfuryl derivatives to produce sulfuryl fluoride (see Table I). The generalized reaction is

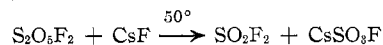


The fate of the new anion,  $\text{X}^-$ , depended on its nature. For example, when peroxydisulfuryl difluoride was heated to  $75^\circ$  in the presence of cesium fluoride, oxygen as well as sulfuryl fluoride was obtained.



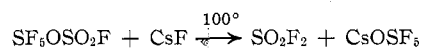
The attack by fluoride ion is believed to occur on the sulfur rather than on oxygen since no fluorine fluorosulfonate or oxygen difluoride was found. The postu-

lated intermediate peroxyfluorosulfonate salt,  $\text{Cs-OOSO}_2\text{F}$ , could not be isolated as it apparently decomposed to oxygen and cesium fluorosulfonate under the experimental conditions. The ratio of oxygen to sulfuryl fluoride found was in good agreement with the above reaction scheme. On the other hand, when pyrosulfuryl fluoride was treated with cesium fluoride at  $50^\circ$  the only volatile product produced was sulfuryl fluoride.



In fact a 50% conversion of pyrosulfuryl fluoride to sulfuryl fluoride was found to occur at  $150^\circ$  in a "clean prefluorinated" monel bomb, whereas no decomposition was noted in glass. The metal fluorides in the bomb were sufficiently active to cause decomposition, presumably in the same manner.

The attack of fluoride ion on the sulfur atom in the sulfuryl group was again demonstrated when  $\text{SF}_5\text{OSO}_2\text{F}$  was heated with cesium fluoride at  $100^\circ$ .



Little or no sulfur hexafluoride was obtained. Thus the attack occurred primarily on the sulfur atom in the sulfuryl group and not on the sulfur atom in the pentafluorosulfur group. After the reaction was complete, fluorine was expanded into the reactor containing the salt residue. Pentafluorosulfur hypofluorite was produced, suggesting the presence of the salt  $\text{CsOSF}_5$ .

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## The Synthesis and Properties of Some Halogen and Interhalogen Addition Compounds of 1,4-Selenothiane

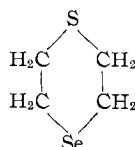
By J. D. McCULLOUGH

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The following halogen and interhalogen addition compounds of 1,4-selenothiane have been prepared:  $\text{C}_4\text{H}_8\text{SSeCl}_2$ ,  $\text{C}_4\text{H}_8\text{S- SeBr}_2$ ,  $\text{C}_4\text{H}_8\text{SSe} \cdot 2\text{I}_2$ ,  $\text{C}_4\text{H}_8\text{SSe} \cdot \text{ICl}$ ,  $\text{C}_4\text{H}_8\text{SSe} \cdot 2\text{ICl}$ ,  $\text{C}_4\text{H}_8\text{SSe} \cdot \text{IBr}$ , and  $\text{C}_4\text{H}_8\text{SSe} \cdot 2\text{IBr}$ . The compositions have been established through combustion analysis for carbon and hydrogen, iodometric determination of equivalent weights, and comparison of the densities computed from single-crystal X-ray diffraction data with those determined by flotation. Probable molecular structures are suggested on the basis of the present and previous X-ray diffraction studies and a knowledge of the dissociation constants of related compounds in solution.

### Introduction

A study of halogen and interhalogen addition compounds of 1,4-selenothiane



provides an opportunity to observe competition of two types. One area of competition is that between selenium and sulfur for the halogen or interhalogen

when the latter are limiting reagents. The other is the competition between tendencies to form more conventional covalent compounds *vs.* tendencies to form molecular or charge-transfer complexes. The present study reports the preparation and characterization of seven halogen or interhalogen addition compounds of 1,4-selenothiane and suggests probable molecular structures for some of them. Complete structural studies of several of the compounds by three-dimensional X-ray diffraction methods are in progress. The results of these studies should provide answers to a number of interesting questions arising from the above competition.