quadrupole broadening in any asymmetrical complexes most likely would prevent the detection of signals at these salt concentrations.

Attempts were made to slow exchange in the 1:1 and 2:1 Cl^- and Br^- systems by cooling the samples to 0°, but a signal still could not be detected. Calibration experiments with InI_4^- solutions showed that below 0°, viscosity broadening would be too severe to observe any peak. Bromine-79 nmr measurements also were made with these solutions, but complex formation with In^{3+} and the resultant quadrupole interactions broadened the signals beyond detection.

Based on the pmr and indium-115 nmr data of this study and the results of Raman[30-32] and indium-115 nmr measurements with similar indium halide systems,[33] the sharp indium-115 signal observed in all halide solutions can be attributed to the particular InX_4^- complex. The Raman spectrum obtained with a pure aqueous InI_3 solution containing excess HI corresponded unambiguously to tetrahedral InI_4^-. Rapid intercomplex exchange and, perhaps, less extensive complexing prevented this observation in aqueous $InCl_3$ and $InBr_3$ solutions, but when these solutions were extracted with ethyl ether, the Raman spectra conclusively identified the presence of only tetrahedral $InCl_4^-$ and $InBr_4^-$. Although the salt and halide concentrations are lower in the present study, the large acetone concentrations and subsequent lowering of the dielectric constant would induce comparable complex formation. The previous indium-115 nmr study[33] revealed (a) a sharp signal for pure aqueous InI_3 solutions, shifted ~583 ppm upfield from a similar $In(ClO_4)_3$ reference peak, (b) one broad signal attributed to In^{3+} complexes undergoing rapid exchange in pure aqueous $InCl_3$ and $InBr_3$ solutions, and (c) single sharp signals shifted 440 and 180 ppm downfield from the reference peak, for ether-extracted solutions of $InCl_3$ and $InBr_3$, respectively. Based on symmetry considerations, the assumption that complexing would be favored in the ether solutions, and the previously cited Raman studies,[30-32] the authors concluded that these sharp signals were due to the tetrahedral InX_4^- complexes.[33] The remarkable similarity of the chemical shifts (and line widths in the solutions of high acetone content) listed in Table II and those reported by Cannon and Richards for the extracted halide solutions means the same species are being observed in each case. Since the dielectric constants of the systems are both low, ~4 in ether and ~20 in the acetone solutions, complexing to a comparable extent would be expected.

Finally, the conclusions of this study may be compared briefly to the results of studies of similar gallium halide solutions.[28,29,37-39] The formation of tetrahedral GaX_4^- complexes was demonstrated in pure aqueous solutions by Raman[37,39] and ion-exchange[39] methods and in water–acetone mixtures by pmr and gallium-69 nmr techniques.[28,29] However, the nmr data were consistent with combinations of GaX_4^- with only $Ga(H_2O)_6^{3+}$, and no evidence was found for significant amounts of intermediate complexes.[28,29] Thus, the complexing tendencies are stronger in the gallium halide solutions.

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Reactions of Lower Fluorides of Sulfur with Hydrogen Sulfide

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The reactions of H_2S with FSSF, SSF_2, SF_4, and SOF_2 were studied at low temperature, and the products were analyzed by nmr spectroscopy. In each case, one or more members of the sulfanes, H_2S_x, were produced. With excess H_2S, the major product is H_2S_4; with deficit H_2S, only $H_2S_{\geq 6}$ is observed. The formation of sulfane is interpreted as resulting from a simple condensation process in the case of FSSF, condensation followed by rearrangement in the case of SSF_2, and formation of SSF_2 as an intermediate step in the case of SF_4.

Introduction

The reaction of SSF_2 with H_2S was reported by Seel and Gölitz[2] to give predominantly sulfur. Under certain unspecified conditions, the products consisted almost entirely of yellow oils. It was suggested that these oils might be fluorosulfanes, FS_nF, by analogy with the known reactions of chlorosulfanes with H_2S.[3]

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(1) Work performed during a stay at the University of Washington.

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Furthermore, Seel studied the reaction of SSF_2 with liquid HF and concluded that it was a two-stage process

$$SSF_2 + 2HF \longrightarrow H_2S + SF_4 \quad (1)$$

$$H_2S + SSF_2 \longrightarrow 3S + 2HF \quad (2)$$

We were interested in studying the reactions of SSF_2 and SF_4 with H_2S under controlled conditions, *i.e.*, at low temperature and in the presence of an inert solvent which acts as a heat sink for exothermic reactions. We wanted to learn more about FSSF, the yellow oil, and the preparation of SSF_2, in order to compare the chemistry of fluorosulfanes with that of other halosulfanes.

Experimental Section

Materials.—Purified sulfur (99.999+%) was a gift of the Freeport Sulfur Co. Hydrogen sulfide (Matheson Co.) was dried over P_2O_5 and pumped free of noncondensable impurities at −196°. Sulfur tetrafluoride (Matheson Co.), SOF_2 (Hynes Chemical Research Co.), and CCl_3F (Matheson Co.) were also pumped free of noncondensable impurities at −196° and then used without further purification. We found by mass spectral analysis that the SF_4 contained 50.3% SOF_2 as received, but no separation was undertaken. Silver fluoride (Alfa Inorganics, Inc.) was dried under high vacuum for 6 hr at 160° before use.

Apparatus.—All manipulations and reactions were effected in borosilicate glass apparatus using standard vacuum techniques. A chlorofluorocarbon lubricant (Halocarbon 25-5S, Halocarbon Products Corp.) was used on stopcocks and ground-glass joints. The proton nmr spectra were obtained using Models T-60 and A-60 (Varian Associates) and the fluorine nmr spectra with Model DA-60-1c (Varian). Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer using a 5-cm glass cell equipped with a Teflon stopcock and silver chloride windows. The windows were sealed to the cell with a chlorofluorocarbon wax (Series 6-00, Halocarbon Products Corp.).

Reaction of Silver Fluoride with Sulfur.—For the preparation of mixtures of FSSF, SSF_2, and SF_4, 3.38 g of sulfur was degassed twice by melting and resolidifying in an ampoule under vacuum and then pumping away any volatiles released during melting. The ampoule was sealed to an inverted ampoule fitted with a break-seal and containing 1.52 g of predried silver(I) fluoride. Between the two ampoules was a side arm equipped with an nmr tube. The entire apparatus was repeatedly flamed out or heated with a hot air gun under vacuum and then the glass seal was broken, thereby allowing the silver fluoride to drop into the sulfur ampoule. This ampoule was then heated in an oil bath to 124° to melt the sulfur. At this temperature, the onset of reaction was indicated by a vigorous bubbling of the mixture, which continued for several hours before subsiding. The products were condensed directly into an nmr tube immersed in liquid N_2 only a few inches from the reaction zone. At the conclusion of the reaction, 1 ml of CCl_3F was distilled into the nmr tube, which was then sealed. The tube was then allowed to warm to −100° at which temperature the ^{19}F nmr spectrum was recorded. This spectrum consisted of two triplets centered at −91.5 and −35.3 ppm with respect to CCl_3F, both assigned to SF_4,[4] together with two considerably more intense peaks, one at −78.3 and the other at 122.7 ppm. These are assigned to SSF_2 and FSSF, respectively.[5] No other peaks were detected. Measurement of peak heights gave the compositions as approximately 38% SSF_2, 36% FSSF, and 26% SF_4. The nmr tube was then allowed to warm to room temperature and after 10 min a second spectrum was recorded. This showed the two SF_4 triplets collapsed to a single broad resonance at −63.4 ppm, the SSF_2 peak now greatly increased in intensity, and the FSSF peak diminished to a very low intensity.

In a similar experiment, with the same weights of sulfur and AgF as before, a weighed tube fitted with a ground-glass joint was attached to the reaction ampoule in place of the nmr tube. The volatile products were condensed in this tube for 5 hr from the onset of reaction. Very little condensed after the first hour. The reaction was stopped by allowing the ampoule to cool below the melting point of sulfur; then the tube containing the products was sealed off and weighed together with the joint that had attached it to the reaction zone. By difference, the weight of the S_2F_2–SF_4 mixture was 0.138 g.

Throughout this paper we use the formula S_2F_2 to represent the approximately equimolar mixture of FSSF and SSF_2 formed by our reaction of silver fluoride with sulfur.

Reaction of S_2F_2 with H_2S. (a) **H_2S in Excess.**—The apparatus, Figure 1, consisted of two concentric cylinders, the inner one forming a cold finger that would contain the refrigerant. The outer cylinder was connected near the top to the vacuum line, while near the bottom were two inlets for the S_2F_2 and H_2S. The bottom of this outer cylinder tapered off to an nmr tube directly below the bottom of the inner well, the latter being pointed to facilitate liquid dripping off into the nmr tube. The S_2F_2 and H_2S inlets were both equipped with jets with a 1-mm diameter orifice angled so that the reagent streams cocondensed on the surface of the cold finger. The ampoule containing the AgF–S mixture, as described above for the preparation of S_2F_2, was connected directly to one of these jets. To the other jet was attached a flowmeter and a bulb containing a mixture of H_2S and CCl_3F vapor. The flowmeter had previously been calibrated for use with this mixture.

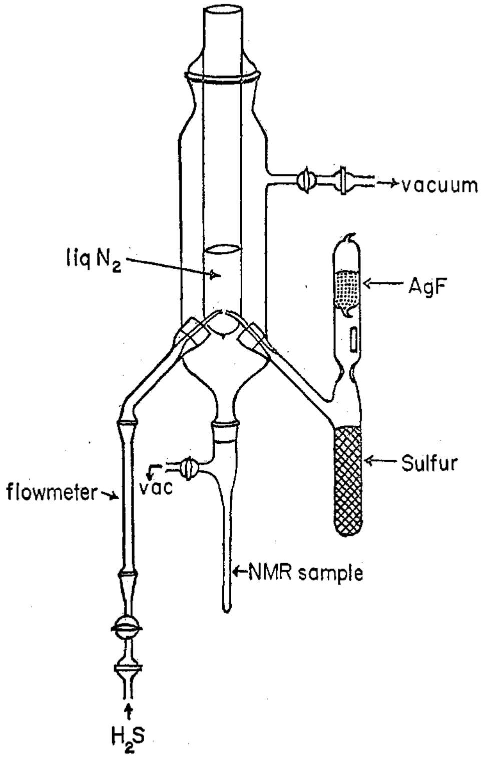

Figure 1.—Apparatus for cocondensing H_2S with lower fluorides of sulfur.

In a typical experiment, 1.58 g of AgF and 3.43 g of S gave, in addition to unreacted reagent, 211 mg of the S_2F_2–SF_4 mixture as measured by weight loss of the ampoule, and this mixture was condensed onto the lower part of the cold finger by using liquid N_2 as a refrigerant. A 5:3 mixture of H_2S and CCl_3F (0.50 g, 14.6 mmol of H_2S) was simultaneously condensed onto the cold finger. Deposition of reagents on the finger took 1 hr, at the conclusion of which the supply of reagents was shut off. The liquid N_2 refrigerant was then rapidly siphoned from the cold finger and replaced by melting isopentane (−160°). This organic slush was allowed to warm slowly while monitoring the temperature with a pentane thermometer. At −150° the white deposit on the cold finger turned yellow. The intensity of this yellow color increased slightly until at −120° the CCl_3F began melting and carrying solid particles to the bottom of the finger. A bath of melting toluene (−96°) was then put around the nmr tube to collect the CCl_3F slurry. When the isopentane in the cold finger had warmed to −40°, the nmr tube was cooled to

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−196° and sealed off. The proton nmr spectrum of this sample showed primarily H_2S_4, with small amounts of H_2S_5 and $H_2S_{\geq 6}$.

The vacuum in the apparatus was then broken and the cold finger was removed. Yellow droplets of product remaining on the finger were dissolved in CS_2 and an ^1H nmr spectrum of the resulting yellow solution was obtained. From this spectrum the composition of the yellow liquid was found to be 86% H_2S_4, 5% H_2S_5, and 9% sulfanes with six or more sulfur atoms (H_2S_4:H_2S_5:$H_2S_{\geq 6}$ = 17:1:2). H_2S was also detected. HF which was always formed was not analyzed.

(b) **S_2F_2 in Excess.**—The apparatus was essentially that used in (a). Instead of the nmr tube below the cold finger, however, a gas-phase ir cell was attached through a ball joint. The experimental procedure was similar to that for an excess of H_2S. A 1.50-g sample of silver fluoride and 3.18 g of S were heated and the products were condensed together with H_2S (0.02 g, 0.4 mmol) and CCl_3F (0.96 g, 6.0 mmol). On warming this mixture, the volatile products were allowed to expand into the ir cell, leaving a brilliant yellow-orange liquid on the cold finger. When the apparatus had reached room temperature, the ir cell was closed off and air was introduced to the rest of the apparatus. The ir spectrum of the volatile residue showed the presence of S_2F_2,[6] SF_4,[7] SOF_2,[8] $CFCl_3$,[9] and some SiF_4.[7] HF absorbed above 4000 cm^{-1} and did not interfere with identification of the other products. The ^1H nmr spectrum of a solution in CS_2 of the less volatile products remaining on the cold finger consisted of a single peak of unresolvable fine structure. This peak was assigned to $H_2S_{\geq 6}$.

Reaction of SF_4 with H_2S, in the Presence of SOF_2. (a) **H_2S in Excess.**—Using the same apparatus as for the reactions of S_2F_2, 2.4 mmol of SF_4 (0.25 g), containing about the same amount of SOF_2, and 17.6 mmol of H_2S (0.60 g) were condensed together at liquid N_2 temperature in the apparatus shown in Figure 1 and then slowly warmed by allowing the liquid N_2 in the cold finger to boil off at its own rate. Formation of a yellow product began at low temperatures. When the apparatus reached room temperature, a sample of the volatile products was analyzed by ir spectroscopy as containing SOF_2, SiF_4, and H_2S. The yellow residues on the cold finger were dissolved in CS_2 and from the ^1H nmr spectrum of the resulting solution the composition of these products was established to be H_2S and 72% H_2S_4, 7% H_2S_5, and 21% H_2S_6 (H_2S_4:H_2S_5:$H_2S_{\geq 6}$ = 10:1:3).

(b) **SF_4 in Excess.**—A 1.97-g sample of SF_4 and 2.3 mmol of H_2S (0.08 g) were allowed to react as in (a). A yellow liquid formed as before, which ^1H nmr analysis identified as 100% $H_2S_{\geq 6}$. The volatile products were identified by ir spectroscopy as SF_4, SOF_2, and SiF_4.

Results and Discussion

We have studied the reactions at low temperatures of SSF_2, FSSF, and SF_4 with varying proportions of H_2S and find that all three fluorides form mixtures of sulfanes, HS_nH, whether there is initially a molar excess or deficit of H_2S. In the case of an excess of H_2S, all three sulfur fluorides give yellow oils containing H_2S_4 as the major component, with lesser amounts of $H_2S_{\geq 6}$ and H_2S_5. When there is an initial deficit of H_2S, however, $H_2S_{\geq 6}$ compounds are the main products. The preferred formation of one sulfane species in each experiment confirms that, under our conditions, sulfanes do not significantly convert.[10,11] However, older samples at room temperature slowly decompose and form mixtures of H_2S_n with $3 < n < 8$. Characterization of these sulfanes was by means of the well-known chemical shifts for H_2S_n, where $n = 1$–6 have been tabulated by Schmidbaur, Schmidt, and Siebert.[12] The chemical shifts of sulfanes with six or more sulfur atoms cannot be resolved on present equipment, because their signals differ by less than 1 Hz. The compositions, as measured from the nmr spectra, of the product oils from typical experiments are shown in Table I.

TABLE I

DISTRIBUTION (%) OF SULFANES IN PRODUCTS OF REACTION OF H_2S WITH SULFUR FLUORIDES

	FSSF–SSF_2–SF_4		SF_4	
	Excess H_2S	Deficit H_2S	Excess H_2S	Deficit H_2S
H_2S_3	. . .	. . .	. . .	. . .
H_2S_4	86	. . .	72	. . .
H_2S_5	5	. . .	7	. . .
$H_2S_{\geq 6}$	9	100	21	100

In forming H_2S_4 as the main product when treated with excess H_2S, FSSF reacts analogously to ClSSCl.[3b] We can, therefore, write the equation for the reaction as

$$\text{HS-H} + \text{F-SS-F} + \text{H-SH} \longrightarrow \text{HS}_4\text{H} + 2\text{HF} \qquad (3)$$

The formation of higher sulfanes can be explained by reaction of H_2S_4 with S_2F_2. Such a secondary reaction is plausible at the H_2S:S_2F_2 ratio of 10:40, which we employed in one experiment, because it is generally observed that an excess of at least 1000:1 has to be used to isolate product molecules in a reacting matrix.[13] However, our FSSF constituted only approximately 37% of a mixture that also contained about 37% SSF_2 and 26% SF_4, but since the reaction of this mixture with H_2S gave sulfanes as the only products, SSF_2 and SF_4 must undergo condensation reactions, too.

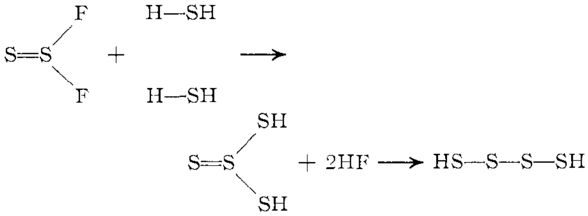
We propose that SF_4 reacts with H_2S with the elimination of HF, just as it reacts with H_2O

$$SF_4 + H_2S \longrightarrow S{=}SF_2 + 2HF \qquad (4)$$

$$SF_4 + H_2O \longrightarrow O{=}SF_2 + 2HF \qquad (5)$$

The SSF_2 thus formed must react very readily with H_2S, because in experiments where H_2S was treated with excess SF_4, no SSF_2 was detected among the volatile products.

The formation of sulfanes from SSF_2 probably involves a rearrangement following condensation and elimination of HF



(6)

The rearrangement step could conceivably give rise to sulfanes other than H_2S_4, depending on the exact mechanism of rearrangement.

In the reactions of the lower fluorides of sulfur with a deficit of H_2S, the main products were sulfanes with a sulfur chain length of six or more. Because the precise chain length of these sulfanes could not be established, we can only speculate about the course of the reactions. Feher investigated the reactions of H_2S and lower sulfanes with excess S_2Cl_2 and found that the major products are chlorosulfanes, formed by condensation

$$\text{ClSSCl} + HS_nH + \text{ClSSCl} \longrightarrow ClS_{n+4}Cl + 2HCl \qquad (7)$$

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We obtained no nmr evidence for the analogous reaction with FSSF, although any higher fluorosulfanes that could have been formed may have decomposed instantaneously on contact with the glass apparatus. However, it is possible that the higher sulfanes constituting our reaction products were formed by the intermediate synthesis of fluorosulfanes, for example

$$2FSSF + H_2S \longrightarrow S_5F_2 + 2HF \tag{8}$$

$$S_5F_2 + 2H_2S \longrightarrow H_2S_7 + 2HF \tag{9}$$

Without a metal vacuum system we were unable to pursue this hypothesis. Similarly, while the mixture of FSSF, SSF_2, and SF_4 could be prepared in glass with no side formation of SOF_2 or SiF_4, attempts to isomerize the FSSF to the more stable[14] SSF_2 isomer were accompanied by considerable SOF_2 formation together with the production of some SiF_4.

Since Moissan and Lebeau[15] had described the reaction of SOF_2 with H_2S upon heating, we treated SOF_2 with an equimolar amount of H_2S at room temperature to determine whether the presence of SOF_2 would interfere with the reactions of sulfur fluorides with H_2S. After 16 hr at room temperature, there had been no detectable reaction between SOF_2 and H_2S. From this we conclude that SOF_2 impurities do not participate in the reaction of SF_4 with H_2S. We further verified this by adding SOF_2 to the SF_4 before reaction with H_2S.

Our work indicates that fluorosulfanes, S_nF_2 with $n > 3$, react very quickly with H_2S. We were unable to observe these species *via* fluorine nmr spectroscopy, in analogy to Seel.[14]

Acknowledgment.—This work was supported by the National Science Foundation (GP-9234). The authors thank Mr. B. J. Nist for recording the ^{19}F nmr spectra.

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Chlorine Monofluoride Addition to Halo Imines. Magnetic Nonequivalence in Some Perfluoro Amines

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Chlorine monofluoride adds to $(CF_3)_2C{=}NCl$, $Cl_2C{=}NF$, $((CF_3)_2C{=}N)_2$, $F_2C{=}NF$, $(CF_3)_2C{=}NF$, and $ClFC{=}NF$ to give $(CF_3)_2FCNCl_2$, $Cl_2FCNFCl$, $(CF_3)_2CFN{=}NCCl(CF_3)_2$ and $((CF_3)_2CFN)_2$, F_3CNFCl, $(CF_3)_2FCNFCl$, and ClF_2CNFCl. The measurably slow nitrogen inversion process in the last two compounds is detected by ^{19}F nmr spectra which show magnetic nonequivalence of fluorines resulting from an asymmetric nitrogen. ClF_2CNFCl gives spectra characteristic of slow inversion at temperatures in excess of 100°. Mercury easily dechlorinates $Cl_nF_{3-n}CNF_{2-x}Cl_x$ ($n = 1$–3, $x = 1, 2$) to corresponding imines.

Chlorine monofluoride is a useful reagent, acting as a fluorinating or chlorinating agent as well as a chlorofluorinating agent.[2,3] Recent papers describe the addition of ClF to carbon–nitrogen multiple bonds giving $>NCl$[4] or $-NCl_2$[5] derivatives. We have found that ClF adds readily to $>C{=}NF$ imines when the carbon substituents are chlorine or fluorine. In some cases, where CF_3 is bonded to the imine carbon, cesium fluoride is required to catalyze the reaction. Each product which contains chlorine bonded to carbon will rapidly lose chlorine at room temperature in the presence of mercury to give $>C{=}NF$ imine. Two of the new compounds, ClF_2CNFCl and $(CF_3)_2FCNFCl$, contain an asymmetric center. At 25° the carbon fluorines of ClF_2CNFCl are magnetically nonequivalent as are the CF_3 groups in $(CF_3)_2CFNFCl$ as detected with ^{19}F nmr.[6] An nmr–temperature study shows hindered inversion about the nitrogen which can be overcome thermally in the case of $(CF_3)_2CFNFCl$ at 60° but is still observed for ClF_2CNFCl at greater than 100°. Most acyclic amines known to invert slowly have a temperature of coalescence below 25°, although there are exceptions.[7,8]

Dechlorofluorination of halodifluoraminomethanes with mercury provides a straighforward route to the formation of fluoro imines. Thus, with NF_2CCl_2CN,[9] the syn and anti isomers ($FN{=}CClCN$) are obtained, as are the imines *syn*- and *anti*-$FN{=}CClF$[10] and $-FN{=}CCl_2$ from NF_2CCl_2F and NF_2CCl_3. Mercury does not react similarly with NF_2CClF_2 apparently because of the stronger carbon–chlorine bond due to the electron-withdrawing properties of the fluorine atoms bonded to carbon. Fluoroimines have been prepared previously from the fluorination of organic nitrogen compounds, the reductive defluorination of $>CFNF_2$ compounds,[11,12] and the dehydrofluorination of $>CHNF_2$ compounds.[11]

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