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Preparation of Phenylsulphur Chloride Tetrafluoride

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PREPARATION OF PHENYLSULFUR CHLORIDE TETRAFLUORIDE

A Thesis
Presented to
the Graduate Faculty
Central Washington State College

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Dennis T. Sauer
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APPROVED FOR THE GRADUATE FACULTY

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ABSTRACT

The reaction of $C_6H_5SF_3$, CsF and Cl_2 was studied under a variety of conditions. The reaction run in the presence of a trace of water yielded $C_6H_5SO_2F$ and $ClC_6H_4SO_2F$. The reaction run in stainless steel at 170°C yielded an amber solid believed to be a polymer with the empirical formula $C_6H_{3.67}SF_2$. Chlorination of a $C_6H_5SF_3$-CsF mixture in monel at 220°C yielded a yellow liquid tentatively identified as a mixture of the new species $C_6H_5SF_4Cl$, $FC_6H_4SF_4Cl$ and $ClC_6H_4SF_4Cl$.

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INTRODUCTION

The chemistry of sulfur fluorides is relatively new, has received much recent attention and promises exciting new developments in the future. A general review of sulfur-fluorine chemistry will be given for an understanding of the present problem. Recent review articles by Cady,[1] George,[2] Roberts[3] and Williamson,[4] as well as more recently reported developments in the field, provide the necessary source information. Since the preparations and reactions of the sulfur fluorides are dependent on the parent sulfur fluorides, SF_2, SF_4 and SF_6, the discussion logically divides into three parts, SF_2 and its derivatives, SF_4 and its derivatives and SF_6 and its derivatives.

SF_2 and Derivatives

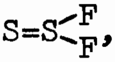
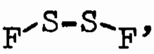
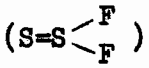
Williamson[4] presents a review of the preparation and chemistry of sulfur difluoride. Table I presents a summary of these preparations. Glemser, Heussner and Haas[6] prepared S_2F_2 as a colorless liquid at -100°C but at -90 to -80°C the liquid turned yellow and formed a gas corresponding to the formula SF_2. Two apparent structural isomers of disulfur difluoride have been reported. Kuczkowski and Wilson[7] identified the compound as thiothionyl fluoride,  $S{=}S\genfrac{}{}{0pt}{}{\diagup F}{\diagdown F}$, while Wilson[8] identified a second isomer of disulfur difluoride,  $_{F}\diagup S{-}S\diagdown_{F}$, via microwave spectral analysis. The only reported derivative of sulfur difluoride is formed by the pyrolysis at 200°C of $(CF_3)_2CFSF_3$ to yield $(CF_3)_2\text{-}CF\text{-}SF$.[10]

TABLE I

PREPARATIONS OF S_2F_2

Reactants	Products	Physical Properties	Reference
$S_2Cl + KSO_2F$	S_2F_2	colorless gas m.p. -165°C b.p. -10°C	5
S + AgF	S_2F_2 and SF_2		6
S + AgF	S_2F_2  $\left(S{=}S\begin{smallmatrix}\diagup F\\ \diagdown F\end{smallmatrix}\right)$	m.p. -165°C b.p. -10°C	7
S + AgF	S_2F_2 $(F{-}S{=}S{-}F)$	b.p. -30°C	8

SF$_4$ and Derivatives

Smith[11] has recently reviewed the preparations and chemistry of sulfur tetrafluoride. These preparations are summarized in Table II.

Sulfur tetrafluoride has a reported melting point of -121°C, boiling point of -38°C and a density of 1.9191 g/cm^3 at 200°K.[17] The structure of the sulfur tetrafluoride molecule is essentially a trigonal bipyramid in which two fluorine atoms and the unshared electron pair are in the equatorial positions with the other two fluorine atoms occupying the axial positions.[20]

TABLE II

PREPARATIONS OF SF_4

Reactants	Products	Reference
$S + CoF_3$	SF_4	12
decomposition of CF_3SF_5	$SF_4 + CF_4$	13
decomposition of S_2F_{10}	$SF_4 + SF_6$	14
$CS_2 + F_2$	SF_4, CF_4, SF_6, CSF_2 CF_3SF_5, CF_3SF_3, $SF_3CF_2SF_5$, $SF_5CF_2SF_5$	15, 16
$S + F_2$	SF_4	17
$S_2Br_2 + IF_5$	$SF_4 + Br_2 + I_2$	18
$S + IF_5$	$SF_4 + I_2$	19
$SCl_2 + NaF$	$SF_4 + S_2Cl_2 + NaCl$	19

Sulfur tetrafluoride is an extremely reactive substance. It is instantly hydrolyzed by water, but its fluorination action is quite selective. Figure 1 summarizes the main reaction types, but does not represent all the reported reactions of SF_4. Sulfur tetrafluoride also converts many metallic oxides or sulfides to the corresponding metal fluorides[23] in reactions similar to the selective fluorination of organic carbonyl groups (Reaction G).

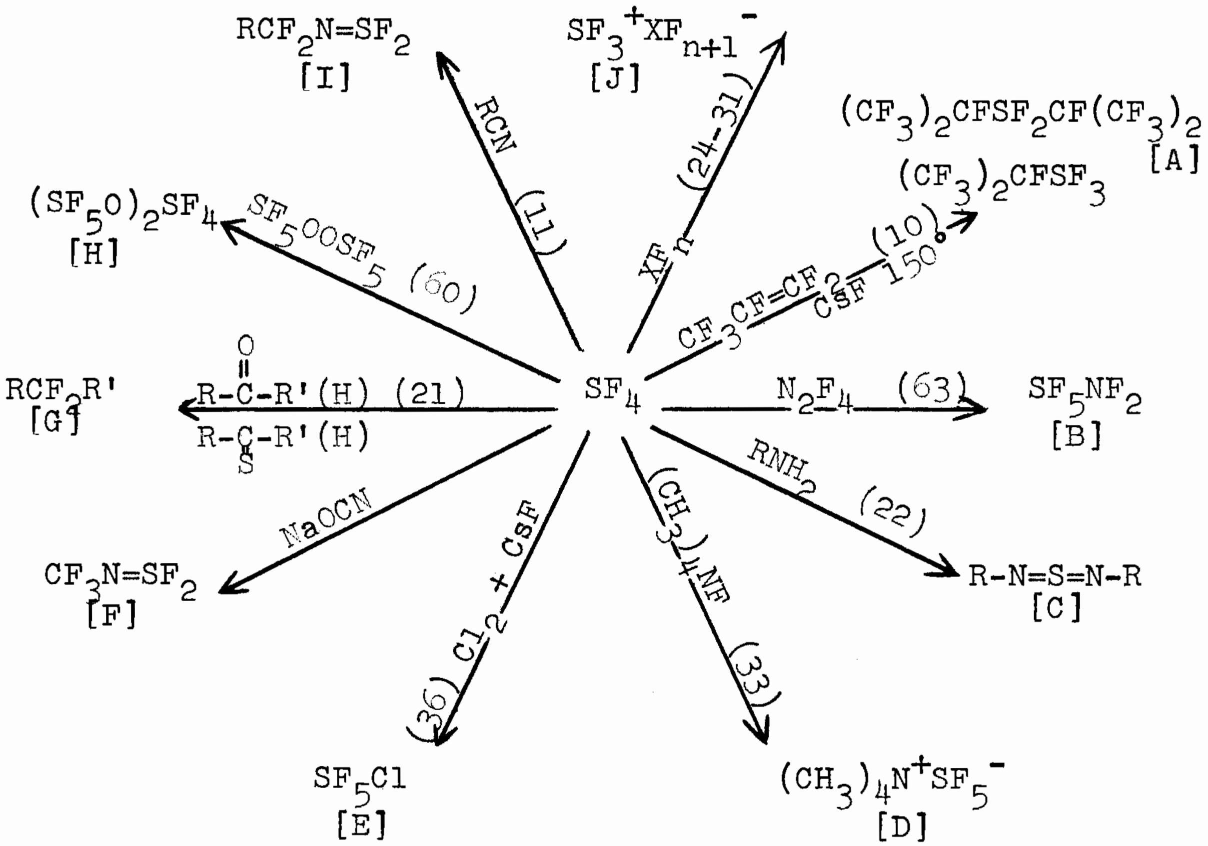


FIGURE I

REACTIONS OF SF_4

The presence of an unshared electron pair in the sulfur tetrafluoride molecule suggests that it should exhibit properties of a base. Similarly, the presence of an unoccupied 3d orbital in the molecule, together with the known ability of the sulfur atom to be hexacoordinate suggests that sulfur tetrafluoride might also be an electron pair acceptor. Actually both donor and acceptor properties have been observed. Sulfur tetrafluoride reacts with certain inorganic fluorides that are Lewis acids to form solid "adducts" (Reaction J). The known adducts in approximate order of decreasing stability are $SbF_5 \cdot SF_4 > AsF_5 \cdot SF_4 > IrF_5 \cdot SF_4 > BF_3 \cdot SF_4 > PF_5 \cdot SF_4 > GeF_4 \cdot 2SF_4$ and $AsF_3 \cdot SF_4$. Early investigators[27] suggested that these substances were simple Lewis acid-Lewis base complexes of the type $SF_4 \rightarrow BF_3$. This was criticized by Cotton and George,[30] who pointed out that phosphorous trifluoride does not react with boron trifluoride and that SF_4 should be a poorer electron donor than PF_3 since the extra fluorine atom would decrease the basicity of the unshared electron pair. This fact and the known ability of SbF_5, AsF_5, IrF_5, BF_3, PF_5, GeF_4 and AsF_3 to accept fluoride ion prompted Cotton and George to suggest a formulation of the type $SF_3^+BF_4^-$. Seel and Detmer[29] have provided more positive evidence for this structure by obtaining an infrared spectrum of the SF_4 BF_3 adduct. The spectrum showed a strong band at 1050 cm^{-1} typical of BF_4^-. The spectrum also showed a doublet at 908 and 940 cm^{-1} which was assigned to the SF_3^+ ion since SF_4 absorbs at 975 cm^{-1}. The acceptor properties of SF_4 were observed in the study of the reaction of chlorine and sulfur tetrafluoride in the presence of cesium fluoride (Reaction E). Muetterties[32] found that at 110°C sulfur tetrafluoride was absorbed on cesium fluoride and postulated the formation of $Cs^+SF_5^-$.

$$CsF + SF_4 \rightleftharpoons Cs^+SF_5^-$$

Since this salt is significantly dissociated at about 150°C, it is necessary to maintain a high sulfur tetrafluoride pressure in a reactor to ensure isolation of a solid that approaches the theoretical 1:1 CsF to SF_4 ratio. Neither Bartlett and Robinson[28] nor Tunder and Siegel[33] observed compound formation in the reaction of CsF and SF_4 in the temperature range of -40°C to 220°C; however, Tunder and Siegel did observe that tetramethylammonium fluoride will react with sulfur tetrafluoride to give $(CH_3)_4N^+SF_5^-$ at -20°C. The product is a solid with 2-3 mm SF_4 pressure at room temperature. The observed effectiveness of larger cations in SF_5^- formation presumably results from a stabilization due to the increased lattice energy of the larger cations.[32] The larger cations will coexist with a large complex anion, otherwise there would be large anion-anion repulsions. The fluoride ion acceptance reaction has been known for some time with SeF_4,[34] but the above two cases are the first observed for sulfur tetrafluoride.

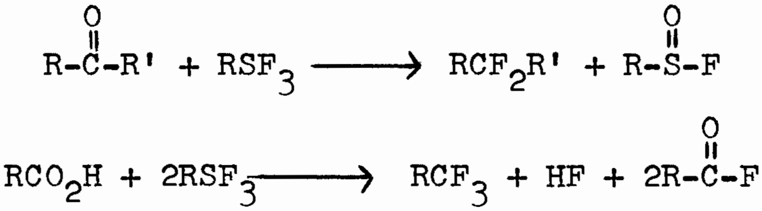
The monosubstituted derivatives of sulfur tetrafluoride are summarized in Table III.

TABLE III

MONOSUBSTITUTED DERIVATIVES OF SF_4

Reagents	Products	Reference
$CS_2 + F_2$	CF_3SF_3	35
$CS_2 + F_2$	$SF_5CF_2SF_3$	35
$CS_2 + F_2$	$SF_3CF_2SF_3$	35
$HSCH_2COOH + F_2$	SF_3CF_2COOH	35
$NO_2-C_6H_4-S-S-C_6H_4-NO_2$ $+ HF + F_2$	$NO_2-C_6H_4SF_3$	36
$R-S-S-R + AgF_2$ $R= C_6H_5$ or C_6H_4X	$R-SF_3$	37
$SF_4 + R_2NH$	F_3SNR_2	22

Kharasch and Chamberlain[36] prepared 2,4-dinitrophenylsulfur trifluoride by reaction of the corresponding disulfide in liquid hydrogen fluoride at 0°C with fluorine diluted with nitrogen. This method was found to be unsatisfactory for the general preparation of arylsulfur trifluorides. Sheppard[37] devised a general method for the preparation of alkyl and arylsulfur trifluorides by reaction of the corresponding disulfides with silver difluoride in freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane). Sheppard found that the reactions of alkyl and arylsulfur trifluorides with compounds containing carbonyl groups closely paralleled those of sulfur tetrafluoride. Williamson[4] in his review stated that the reactions of alkyl and arylsulfur trifluorides parallel those of SF_4. These reactions were predicted because at the time experimental evidence did not substantially support this statement. There have been no reported acceptor or donor properties of alkyl or arylsulfur trifluorides ($R-SF_2^+$ or RSF_4^- type species) that parallel those found for sulfur tetrafluoride. Sheppard[37] has used the substituted tetrafluorides for selective conversion of carbonyl and carboxyl groups to difluoromethylene and trifluoromethyl groups. In particular, phenylsulfur trifluoride has been



$$R-\overset{O}{\overset{\|}{C}}-R' + RSF_3 \longrightarrow RCF_2R' + R-\overset{O}{\overset{\|}{S}}-F$$

$$RCO_2H + 2RSF_3 \longrightarrow RCF_3 + HF + 2R-\overset{O}{\overset{\|}{C}}-F$$

used to advantage for small scale preparations since the reaction may be run in glass, metal or polyethylene containers at atmospheric pressure.[38] In contrast, sulfur tetrafluoride reactions require pressure equipment constructed of fluorine resistant material.[19, 39]

SF_6 and Derivatives

Roberts[3] reviewed the preparative procedures for producing sulfur hexafluoride. Table IV presents a summary of these preparations.

TABLE IV

PREPARATIONS OF SULFUR HEXAFLUORIDE

Reactants	Products	Reference
$S + F_2$	SF_6	40
$S + F_2$	SF_6	41
$MF + S + Cl_2$	$SF_6 + MCl$	42
SF_4 (pyrolysis at 500-1000°)	$SF_6 + S$	43
$SF_4 + HF$ (electrolysis)	$SF_6 + H_2$	43

Chemically, sulfur hexafluoride is almost totally inert. The reactions of SF_6 are shown in Figure 2. Padma and Murthy[47] reported that sulfur hexafluoride was reduced to H_2S by hydrogen iodide at room temperature. This reaction has since been studied by other investigators[48] with conclusive evidence the reaction does not occur. Two groups have reported the reaction of SF_6 with sodium. Cowan, Riding and Warhurst[44] reported the formation of NaF and S_2F_{10} in a solventless system. Demitras and McDiarmiel[46] studied the reaction in diglyme and proposed that the reaction proceeds due to an electron transfer from a diphenyl radical ion to a SF_6 molecule. Presumably the resulting SF_6^- ion would be unstable since no compound containing this ion has been isolated. It could eliminate F^-, and the $\cdot SF_5$ species so formed would react further with the sodium "solution" to yield the reaction products, Na_2S and NaF.

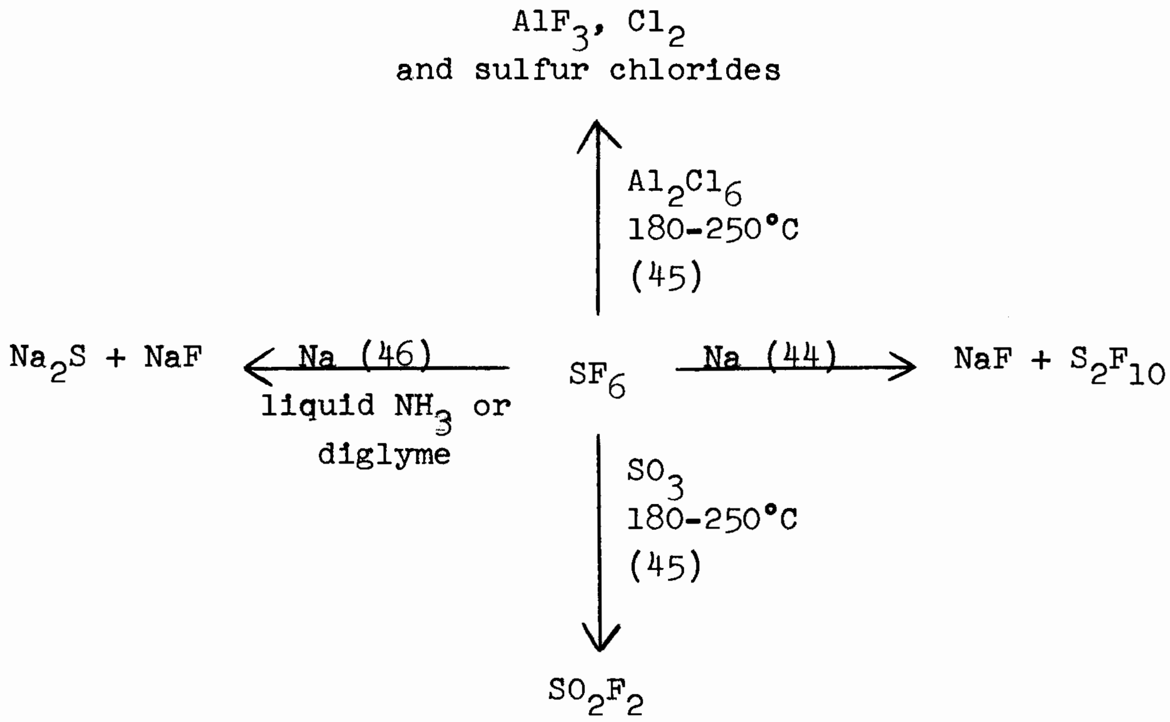


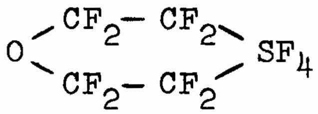
FIGURE 2

REACTIONS OF SF_6

The structure of sulfur hexafluoride is octahedral, as would be expected for sp^3d^2 hybridization. The structure has been established by electron diffraction[50] with the six S-F bond lengths measuring 1.56 Å. Infrared spectra[51] and nuclear magnetic resonance[52] spectra support the octahedral structure.

The monosubstituted derivatives of sulfur hexafluoride have been studied extensively by several research groups including Muller, Lauterbur and Svatos,[53] Harris and Packer,[54] and Merrill, Williamson, Cady and Eggers.[55] Table V is a summary of the monosubstituted derivatives reported.[55]

Two groups bonded to sulfur tetrafluoride produce geometrical isomers of a six-coordinate sulfur derivative. The disubstituted derivatives are summarized in Tables VI and VII. Electrochemical fluorination has been used in preparing the exclusively trans-oriented compounds cited in Table VI. Only $CF_3SF_4NF_2$ was prepared by Logothetis, Sausen and Shozda[63] from the reaction of CF_3SF_3 and tetrafluorohydrazine and found to be exclusively trans-oriented. Only one cis-oriented derivative,



has been prepared by electrochemical fluorination. Shreeve and Cady[59] were the first to obtain a disubstituted derivative by means other than electrochemical fluorination.

TABLE V

MONOSUBSTITUTED DERIVATIVES OF SF_6

Reported Derivatives	
SF_5Cl	SF_5Br
SF_5SO_3F	SF_5OF
$(SF_5)_2SO_4$	$C_2F_5OSF_5$
$C_5F_9OSF_5$	$FC_2Cl_4OSF_5$
CF_3OSF_5	SF_5OSF_5
CF_3SF_5	$C_2F_5SF_5$
$FC_2H_4OSF_5$	$FClC_2H_3OSF_5$
$C_6H_5OSF_5$	NH_2SF_5
RSF_5* (R = C_6H_5 or C_6H_4X)	

*Sheppard[56] describes a general method for preparing arylsulfur pentafluorides.

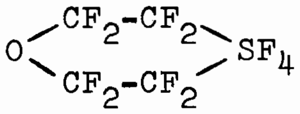
TABLE VI

TRANS-DISUBSTITUTED DERIVATIVES OF SF_6

Derivative	Reference
$(CF_3)_2SF_4$	58
$CF_3SF_4SF_4CF_3$	55
$CH_3SF_4CH_2F$	55
$CF_3SF_4CF_2SF_5$	55
$C_3F_7C_3F_7SF_4$	55
$(C_4F_9)_2SF_4$	55
$CF_3CF_2SF_4CF_3$	55
$(CF_3CF_2)_2SF_4$	55
$CF_3CF_2SF_4SF_4CF_2CF_3$	55
$CF_3SF_4CF_2CFO$	55
$C_3F_7SF_4CF_3$	55
$CF_3SF_4NF_2$	63

TABLE VII

CIS-DISUBSTITUTED DERIVATIVES OF SF_6

Derivative	Reference
	55
$(FSO_3)_2SF_4$	59
$(F_5SO)_2SF_4$	60
$(CF_3O)_2SF_4$	61
$CF_3OSF_4NF_2$	62

They obtained cis-$(FSO_3)_2SF_4$ from the reaction of FSO_2OOSO_2F and SF_4. Other cis-oriented derivatives have since been prepared by similar reactions (Table VII).

Generally, the derivatives of sulfur hexafluoride are chemically inert excepting the mixed halides, sulfur chloride pentafluoride (SF_5Cl) and sulfur bromide pentafluoride (SF_5Br). The mixed halide, SF_5Cl, has been prepared in a number of ways. Table VIII is a summary of these preparations.

SF_5Cl is also an important reaction intermediate as shown in Figure 3. Thermally, SF_5Cl is somewhat more stable than disulfur decafluoride. It is recovered unchanged after being heated to 350°C in an inert container, but at

400°C it decomposes to sulfur hexafluoride, sulfur tetrafluoride and chlorine.[68]

$$2SF_5Cl \xrightarrow{\Delta} SF_6 + SF_4 + Cl_2$$

Hydrolytically it is less stable, being rapidly hydrolyzed by aqueous sodium hydroxide.

$$SF_5Cl + 8NaOH \longrightarrow Na_2SO_4 + 5NaF + NaCl + 4H_2O$$

TABLE VIII

PREPARATIONS OF SF_5Cl

Reactants	Products	Reference
SCl_2 + HF (electrolysis)	$SF_5Cl + H_2$	66
$S_2F_{10} + Cl_2$	SF_5Cl	67
$SCl_2 + F_2$	SF_5Cl	68
$ClF + SF_4$	SF_5Cl	69
$SF_4 + CsF + Cl_2$	$SF_5Cl + CsCl$	36
$NOCl + NaF + SF_4$	$NaCl + SF_5Cl + NO$	70

Since the chemistry of SF_5Cl readily provides reaction paths for the synthesis of monosubstituted derivatives of SF_6 (Figure 3), the preliminary preparation of a similar disubstituted compound could feasibly provide the synthesis of corresponding disubstituted derivatives by similar reactions.

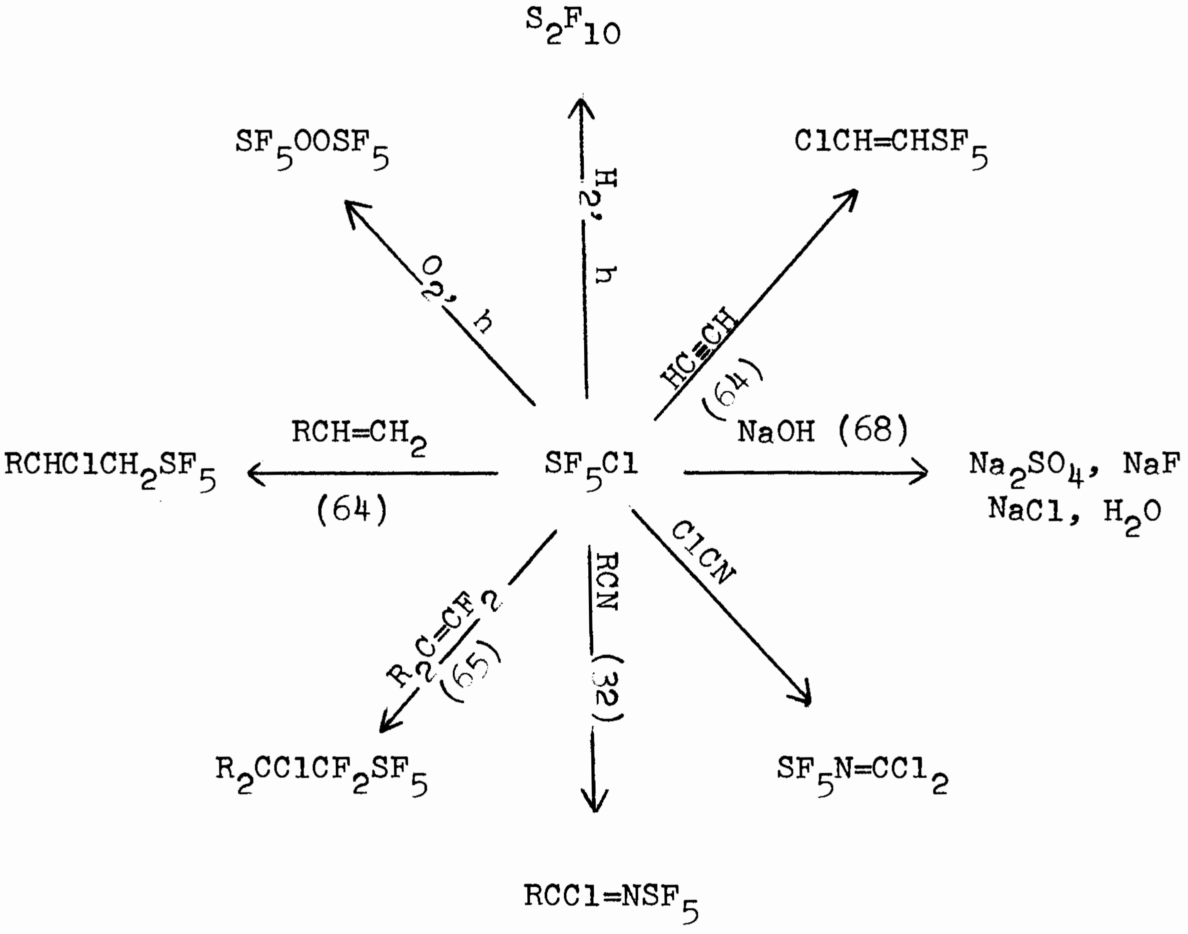


FIGURE 3

REACTIONS OF SF_5Cl

Statement of Problem

The monosubstituted halide derivatives of sulfur hexafluoride, SF_5Cl and SF_5Br, have been employed as useful intermediates for the preparation of other SF_5 containing species. In these reactions, the reactive S-Cl or S-Br bonds can be cleaved with pseudohalogen-like addition of SF_5X to a variety of compounds (Figure 3).

In 1962, Sheppard reported the preparation of $C_6H_5SF_3$ and $C_6H_5SF_5$.[37, 56] The sulfur VI compound is chemically inert and thermally stable while the sulfur IV compound ($C_6H_5SF_3$) seems to show analogous chemistry to the parent SF_4. In both species, the C-S bond seems to be non-reactive.

The purpose of this study was to investigate the chemistry of $C_6H_5SF_3$ and to prepare phenylsulfur chloride tetrafluoride ($C_6H_5SF_4Cl$). There have been no di-substituted sulfur IV halides reported to date. Since the chemistry of $C_6H_5SF_3$ seems to be analogous to SF_4, a logical route to the synthesis of $C_6H_5SF_4Cl$ would be a reaction similar to the preparation of SF_5Cl in which SF_4 is reacted with CsF and Cl_2 to obtain the desired product.[32]

APPARATUS

Vacuum System

Several operations were carried out using a glass vacuum system. Vacuum was achieved using a mercury diffusion pump backed by a mechanical fore pump. System pressures were estimated using a mercury manometer or a tilting McLeod gauge. High vacuum stopcocks were lubricated with Kel-F No. 90 grease (Minnesota Mining and Manufacturing Company). Glass (teflon needle) valves (Fisher-Porter Company) were used in some cases to avoid sample-grease contact.

Reaction Vessels

Reaction vessels of glass, teflon and metal were used. The glass reaction system is described in Figure 7. A 125 ml Nalgene teflon bottle was used as a teflon reactor. The two metal reactors used were a 30 ml Hoke 303 stainless steel reactor (4HS30) and a 95 ml Hoke monel cylinder (4HSM95) each topped with a teflon-packed 316 stainless steel needle valve (Hoke 10115-1). Vacuum tight metal-glass seals were made using a teflon seated "Swagelok" and connecter.

Handling of Compounds

Many of the reagents used in this study were moisture sensitive. Such materials were contained in pre-dried vessels. All mechanical transfers were made in a nitrogen filled polyethylene enclosure (Instruments for Research and

Industry). The nitrogen (Industrial Air) was dried by passage through a 125 cm column packed with anhydrous $CaSO_4$ and P_4O_{10}. An open container of barium oxide was also placed in the enclosure as a dessicant.

Volatile compounds were handled by standard vacuum procedures.

Separation Techniques

Liquid mixtures were separated by distillation. When distilling at reduced pressure, a semi-micro distillation apparatus of 25 ml capacity was used. A capillary bleed from a source of dry air or nitrogen was employed to control superheating in these cases.

ANALYTICAL TECHNIQUES

Spectroscopy

Infrared spectra were obtained using a Perkin-Elmer 137 or Perkin-Elmer 521 spectrophotometer. Samples were examined in a 0.10 mm sodium chloride constant thickness cell or neat between two sodium chloride or potassium bromide plates.

Mass spectral data was obtained on an Associated Electrical Industries MS 10 mass spectrometer. Certain samples were identified using an Associated Electrical Industries MS 9 high resolution mass spectrometer and a Varian Model 4311 B high resolution nuclear magnetic resonance spectrometer with a 40 Mc oscillator.

Organic Qualitative Analysis

Qualitative analyses for sulfur, chlorine and fluorine were carried out by standard methods after the samples were fused with sodium metal.[71, 72]

The presence of sulfur[71, 72] was indicated in the fused material by the formation of a lead sulfide precipitate on addition of lead ion, the observation of a purple coloration when a drop of sodium nitroprusside was added to a portion of fusion filtrate, and by the formation of a silver sulfide stain on the surface of a silver coin when placed in contact with the fusion liquid.

Chloride[71, 72] was detected by acidifying a portion of the fusion liquid, boiling to remove sulfide or cyanide ions and adding silver nitrate solution to form a white silver chloride precipitate.

Fluoride ion[73] was detected by addition of a drop of fusion filtrate to an acetic acid-acetate buffered solution of lanthanum chloranilate (lanthanum salt of 2,5-dichloro-3,6-dihydroxy-p-benzoquinone). The development of a pink to light violet color indicated the presence of fluoride ion.

Quantitative Chemical Analysis

Fluoride ion was determined by titration with standardized thorium nitrate solution using sodium alizarine sulfonate as a visual indicator.[74] Fluoride ion concentration was also estimated by a potentiometric titrametric method[75] utilizing an Orion model 94-09 fluoride specific ion electrode and a Leeds and Northrup expanded scale pH meter. Lanthanum nitrate was used as titrant, the titrations were reproducible with a precision of better than ± two percent. See Figure 4 for a typical titration curve.

Chloride ion concentrations were estimated using standard gravimetric chloride procedures[76] after sample fusion with sodium.

Molecular Weights

Molecular weights were estimated by a standard cryoscopic freezing point depression method using benzene as solvent.[77] Molecular weights were also estimated by identification of the parent peak in a mass spectrum.

REAGENTS

Phenylsulfur trifluoride was obtained as a product in the reaction of phenyl disulfide (Eastman Chemical Company or City Chemical Corporation*) with silver II fluoride (Harshaw Chemical Company) in 1,2,2-trichloro-1,1,2-trifluoroethane (Matheson Chemical Company) at 35-45°C.[37]

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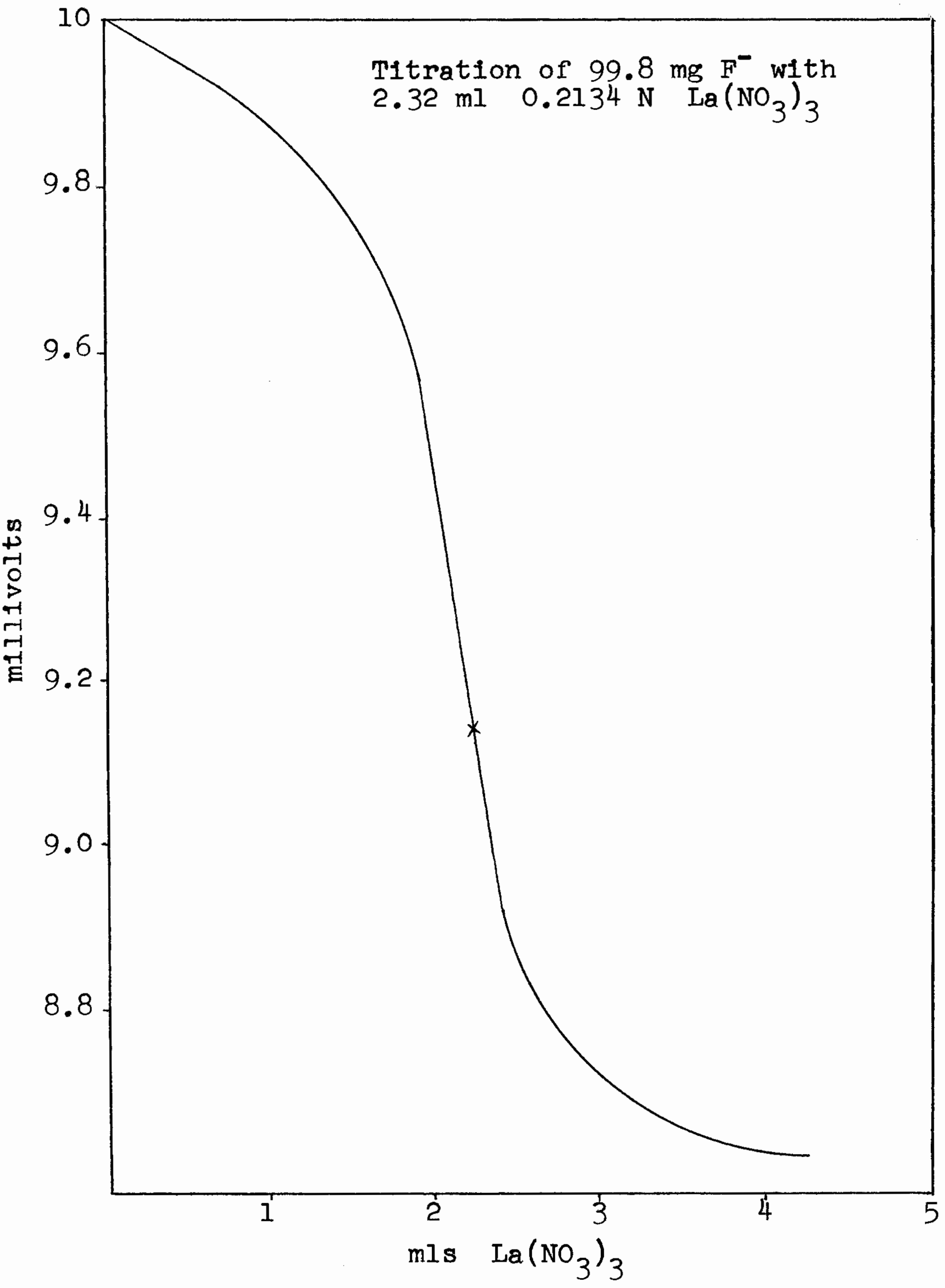
*The phenyl disulfide obtained from City Chemical Corporation contained impurities and was considered to be inferior to that obtained from Eastman Chemical Company.

FIGURE 4

TYPICAL FLUORIDE SPECIFIC ION ELECTRODE TITRATION CURVE



$$12AgF_2 + C_6H_5\text{-}S\text{-}S\text{-}C_6H_5 \longrightarrow 12AgF + 2C_6H_5SF_3$$

1,2,2-trichloro-1,1,2-trifluoroethane will be referred to as "freon 113" throughout the following discussions.

Anhydrous (99.9%) cesium fluoride was purchased from American Potash and Chemical Company. Chlorine was purchased from Hooker Chemical Company and was dried by passage through a 100 cm column packed with anhydrous calcium sulfate or by first bubbling it through concentrated sulfuric acid and then passing it over BaO and P_4O_{10}. Anhydrous (99.9%) sodium fluoride (J. T. Baker Chemical Company) was used as a primary standard for the volumetric standardization of solutions of lanthanum nitrate (Matheson Chemical Company) and thorium nitrate (J. T. Baker Chemical Company).

Baker Analyzed Reagents, $(CH_3)_4NCl$ and HF (48.9% aqueous solution), were used in the attempted preparation of tetramethylammonium fluoride, $(CH_3)_4NF$.

REACTIONS

I. Preparation of Phenylsulfur Trifluoride

The method of Sheppard[37] was used in the preparation of $C_6H_5SF_3$, according to Equation (1).

$$(1)\quad 12AgF_2 + C_6H_5\text{-}S\text{-}S\text{-}C_6H_5 \longrightarrow 12AgF + 2C_6H_5SF_3$$

In a typical preparative run, 15 gm of phenyl disulfide was slowly added to a slurry of 67.2 gm of silver (II) fluoride in "freon 113" through a solid addition funnel. The rate of phenyl disulfide addition was controlled to maintain a reaction temperature of 35-40°C ($C_6H_5SF_5$ has been reported to form under more vigorous conditions).[56] After addition of the phenyl disulfide, the reaction mixture was heated to 47°C for approximately 15 minutes to ensure completion of the reaction. The crude material was then filtered to remove silver (I) fluoride. Solvent was removed by distillation at 47°C and the remaining material vacuum distilled. The colorless product (b.p. 60°C at 5 mm Hg) of 5.2 grams was retained in teflon or stainless steel cylinders for use as "phenylsulfur trifluoride". In the later phases of this work, the preparative procedure was somewhat modified in order to improve the yield.

Phenylsulfur trifluoride reacts slowly with glass and is hydrolyzed rapidly by water (Equations 2 and 3).

$$(2)\quad 4HF + SiO_2 \text{ (glass)} \longrightarrow H_2O + SiF_4$$

$$(3)\quad H_2O + C_6H_5SF_3 \longrightarrow C_6H_5SOF + 2HF$$

Since preparative reactions were run in glass, small amounts of HF formed would lower the yield of phenylsulfur trifluoride considerably. Any C_6H_5SH present would also lead to reduced yields in the same manner (Equation 4).

$$(4)\quad C_6H_5SH + 4AgF_2 \longrightarrow C_6H_5SF_3 + HF + 4AgF$$

The revised preparation used in the later stages of this work was similar to Sheppards[37] except that all operations in the synthesis were run in the presence of excess anhydrous NaF which acted to absorb any HF formed (Equation 5).

$$(5)\quad HF + NaF \longrightarrow NaHF_2$$

II. Phenylsulfur Trifluoride Characterization

The material believed to be $C_6H_5SF_3$ had an infrared spectrum (Figure 5) similar to that reported by Sheppard[37] with the characteristic S-F stretch at 809 cm^{-1}. A sample was hydrolyzed by addition of water (Equations 6 and 7).

$$(6)\quad C_6H_5SF_3 + H_2O \longrightarrow C_6H_5SOF + 2HF$$

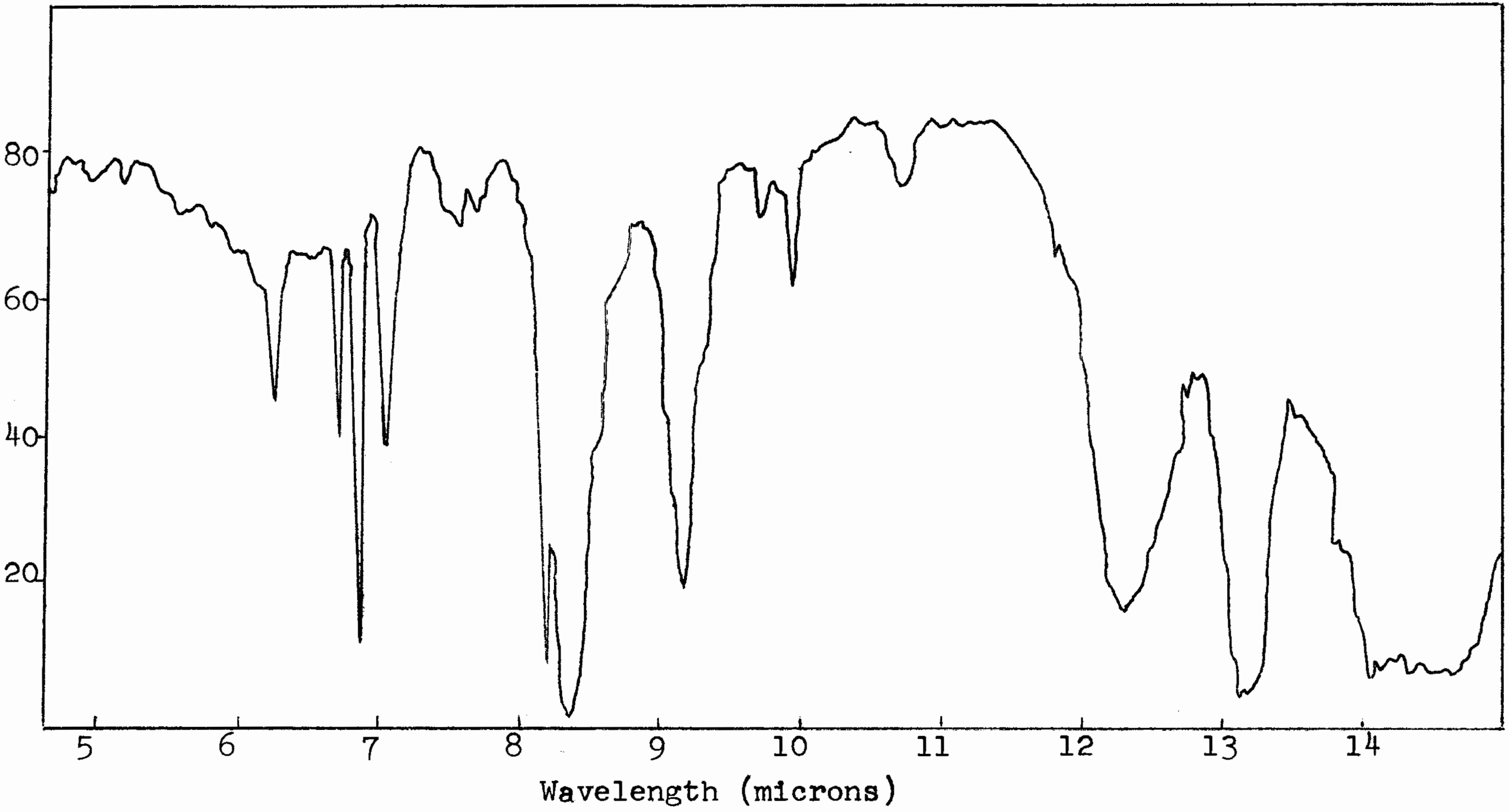


FIGURE 5

INFRARED SPECTRUM OF $C_6H_5SF_3$

$$(7) \quad 2C_6H_5SOF + 2H_2O \longrightarrow 2HF + 2C_6H_5SO_2H$$

The resulting solution was neutralized with dilute sodium hydroxide. Fluoride ion was then titrated with a 0.2134 M lanthanum nitrate solution. The characterized samples were found to be about 70% pure (Figure 6) assuming the only impurity to be C_6H_5SOF. Weights of $C_6H_5SF_3$ in the following reactions are approximately 70% $C_6H_5SF_3$ and will be referred to as "phenylsulfur trifluoride".

III. Reaction of $C_6H_5SF_3$, CsF and Cl_2 in Glass

A reaction vessel (Figure 7) was charged with 16.5 gm (0.0994 mole) of "phenylsulfur trifluoride", 11.4 gm (0.075 mole) of cesium fluoride* and 60 ml of "freon 113". Chlorine was bubbled through the mixture for 30 minutes at a flow rate of about 1.5 l/hr while the solution was stirred vigorously. After 30 minutes, the mixture was heated to reflux (47°C) for an additional 15 minutes. A distillation head was introduced into the system and the "freon 113" removed at 47°C. The reaction vessel was heated to 80°C and chlorine was passed over the remaining residue for an additional 15 minutes. The system was evacuated and a colorless liquid distilled at 78°C/9 mm Hg. The liquid was purified by vacuum distillation. Qualitative elemental analysis of the

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*Cesium fluoride was used directly from the reagent bottle under a nitrogen atmosphere.

FIGURE 6

PURITY OF "$C_6H_5SF_3$"

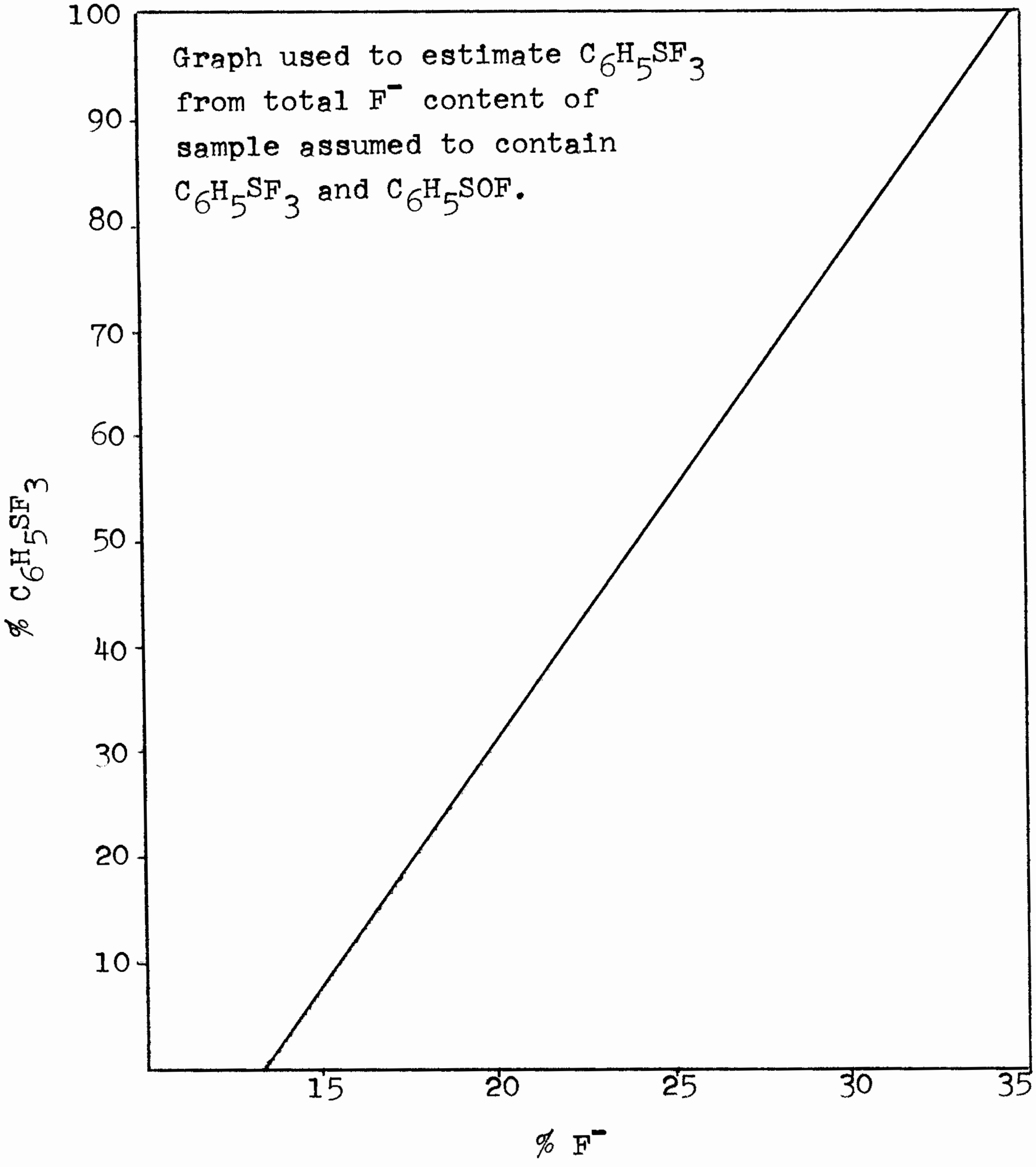
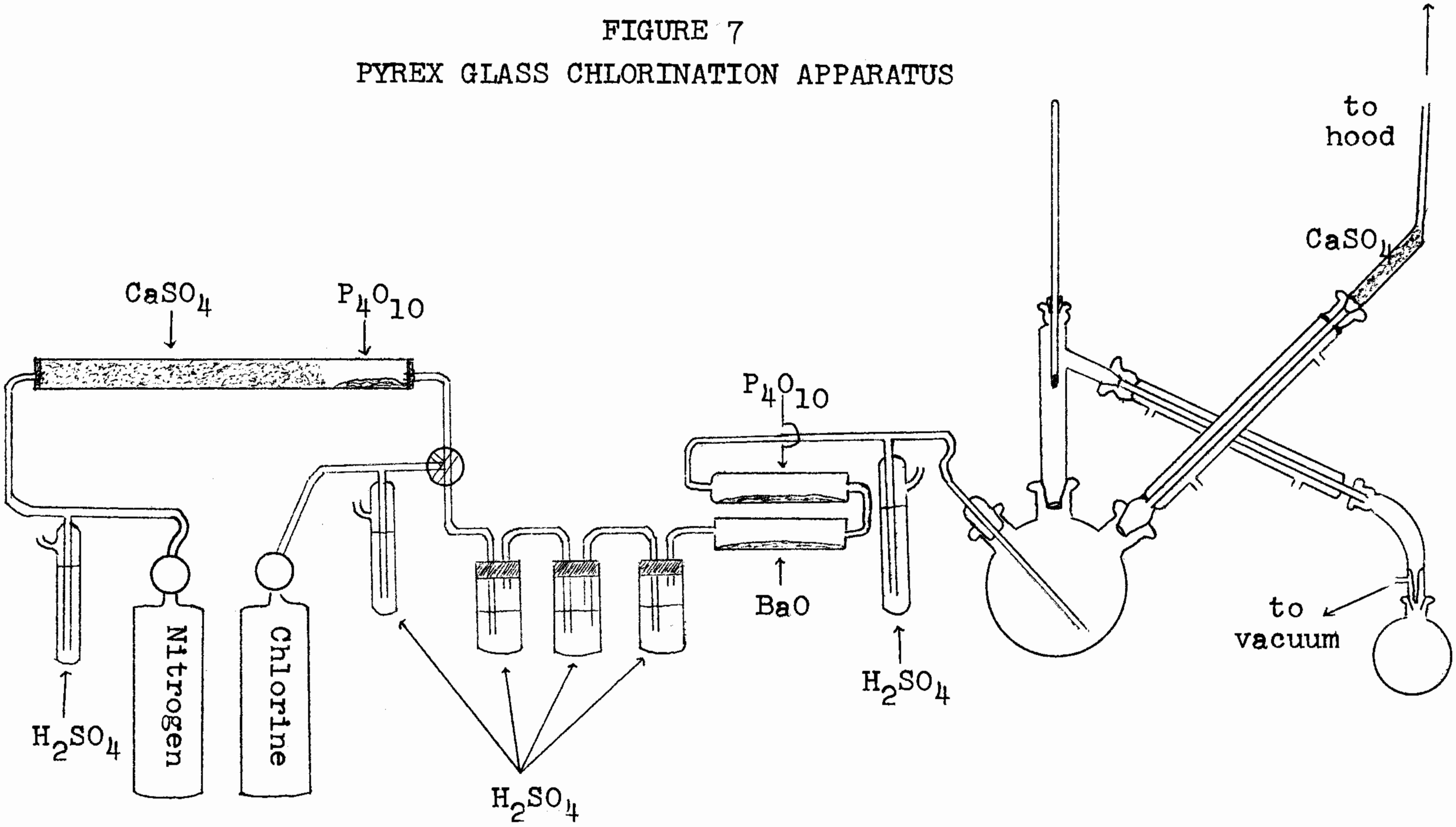


FIGURE 7

PYREX GLASS CHLORINATION APPARATUS



liquid indicated the presence of sulfur, fluorine and chlorine. An infrared spectrum of the compound (Figure 8) corresponded to the reported infrared spectrum[79] for benzenesulfonyl fluoride ($C_6H_5SO_2F$). The mass spectrum of the compound (Table IX) indicated the presence of a monochlorinated benzenesulfonyl species.

TABLE IX

MASS SPECTRUM OF $C_6H_5SO_2F$ (70 V)

m/e	Assigned species	Intensity* relative to $C_6H_5^+$
195.5	$ClC_6H_4SO_2F^+$	0.005
160	$C_6H_5SO_2F^+$	0.179
96	$C_6H_5F^+$	0.464
77	$C_6H_5^+$	1.000
65	$C_5H_5^+$	0.815
51	$C_4H_3^+$	0.888
50	$C_4H_2^+$	0.420
39	$C_3H_3^+$	0.195

*There is a certain degree of uncertainty in assignment of mass units and intensity when using the MS 10 mass spectrometer. Because of this uncertainty only peaks with an intensity of greater than 0.15 relative to the base peak will be assigned.

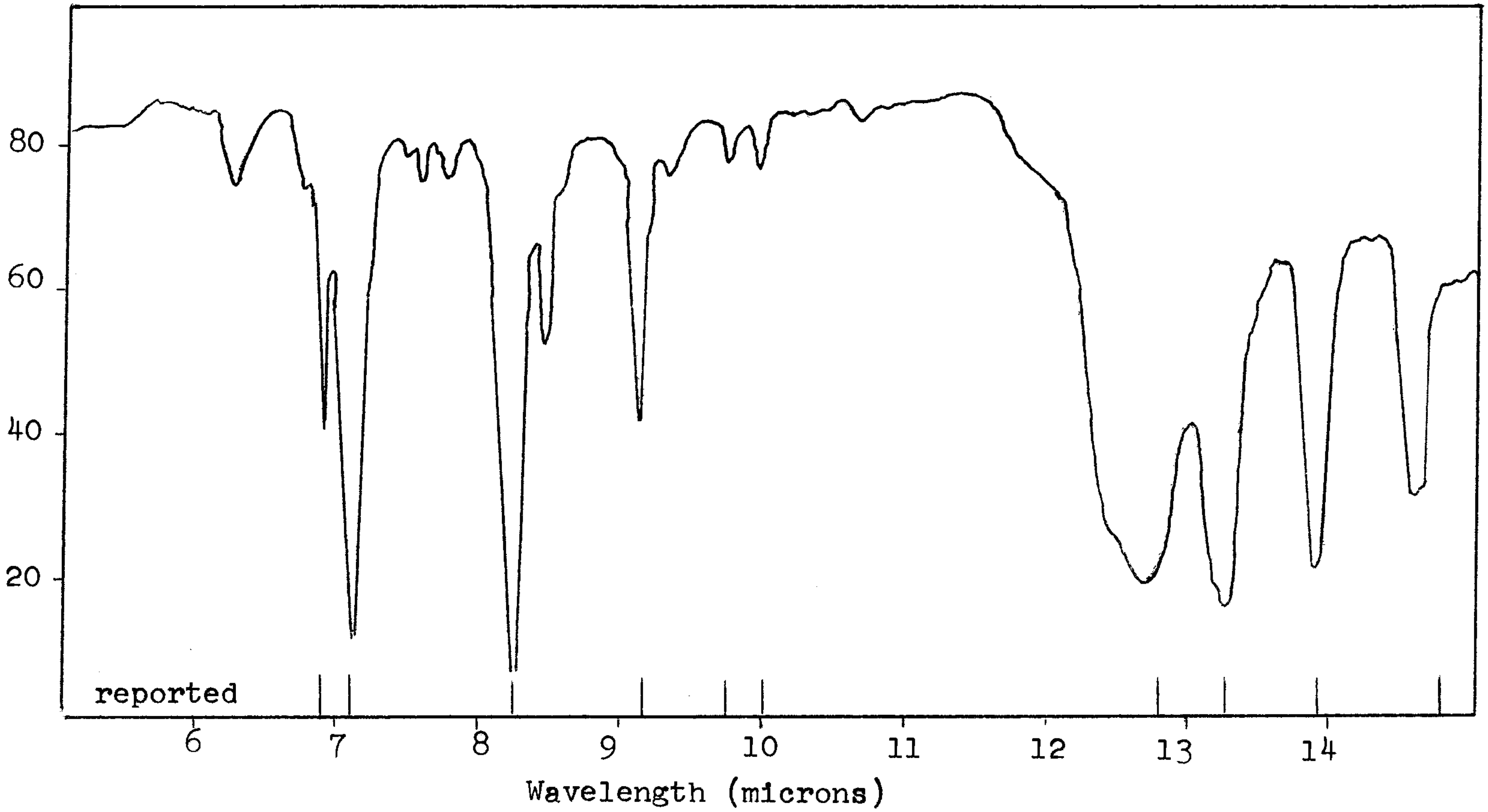


FIGURE 8

INFRARED SPECTRUM OF $C_6H_5SO_2F$

IV. Reaction of $C_6H_5SF_3$, CsF and Cl_2 in Glass

The previous reaction (III) was repeated with 15 gm (0.0984 mole) cesium fluoride and 16.6 gm (0.0997 mole) $C_6H_5SF_3$ in "freon 113" yielding a colorless liquid identified by infrared spectral analysis as benzenesulfonyl fluoride.

V. Reaction of $C_6H_5SF_3$, CsF and Cl_2 in Teflon

A teflon bottle was introduced into the system for use as a reactor to avoid $C_6H_5SF_3$-glass contact (Figure 9). The teflon bottle was charged with 2.74 gm (0.018 mole) cesium fluoride and 3 gm (0.018 mole) $C_6H_5SF_3$ under a nitrogen atmosphere. The mixture was chlorinated for 30 minutes at 45°C and for two hours at 100°C. The resulting mixture was distilled at reduced pressure (b.p. 60-62°C at 3 mm Hg) yielding 1.35 gm (0.0084 mole) of a liquid identified by infrared spectral analysis as benzenesulfonyl fluoride.

VI. Reaction of $C_6H_5SF_3$ and CsF

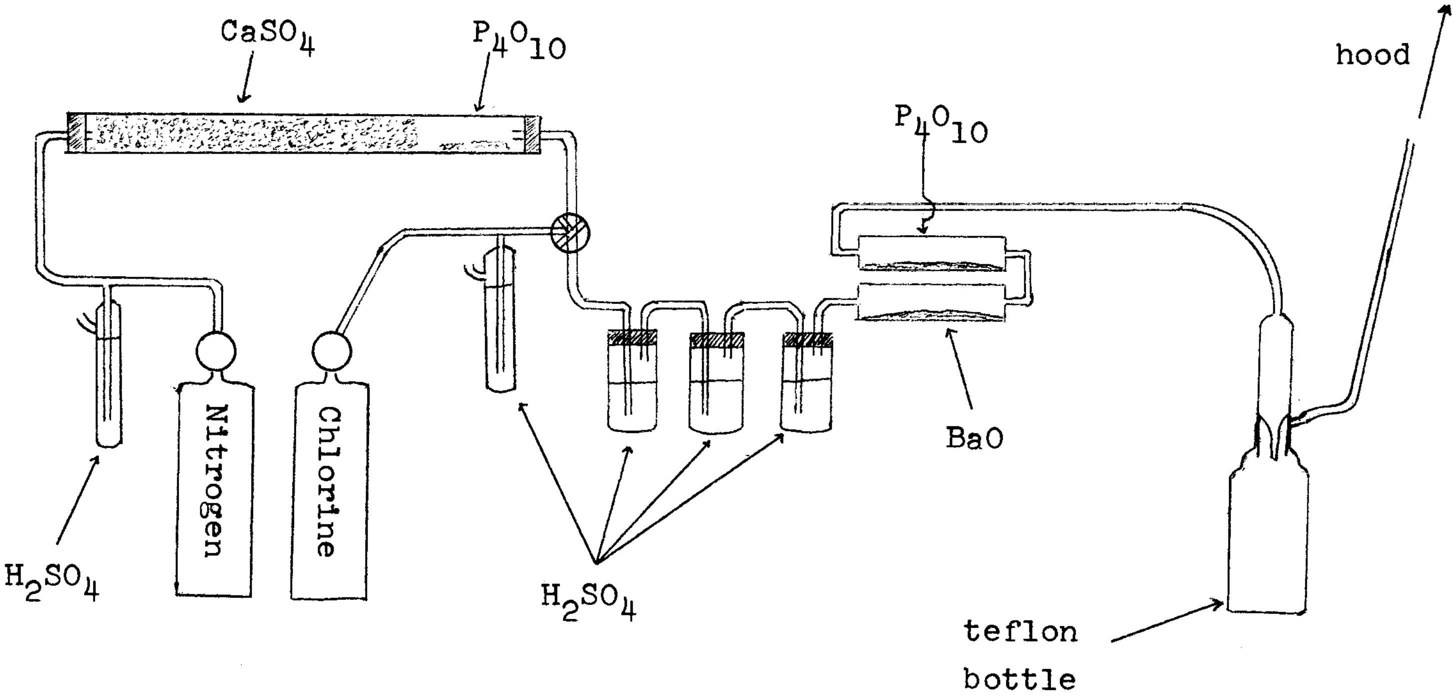
An unmeasured amount of $C_6H_5SF_3$ was vacuum distilled into a receiver containing an excess of cesium fluoride. An infrared spectrum of the liquid in the resulting mixture corresponded to that of unreacted $C_6H_5SF_3$.

VII. Preparation of $(CH_3)_4NF$

$(CH_3)_4NF$ was prepared by a method reported by Tunder

FIGURE 9

TEFLON CHLORINATION SYSTEM



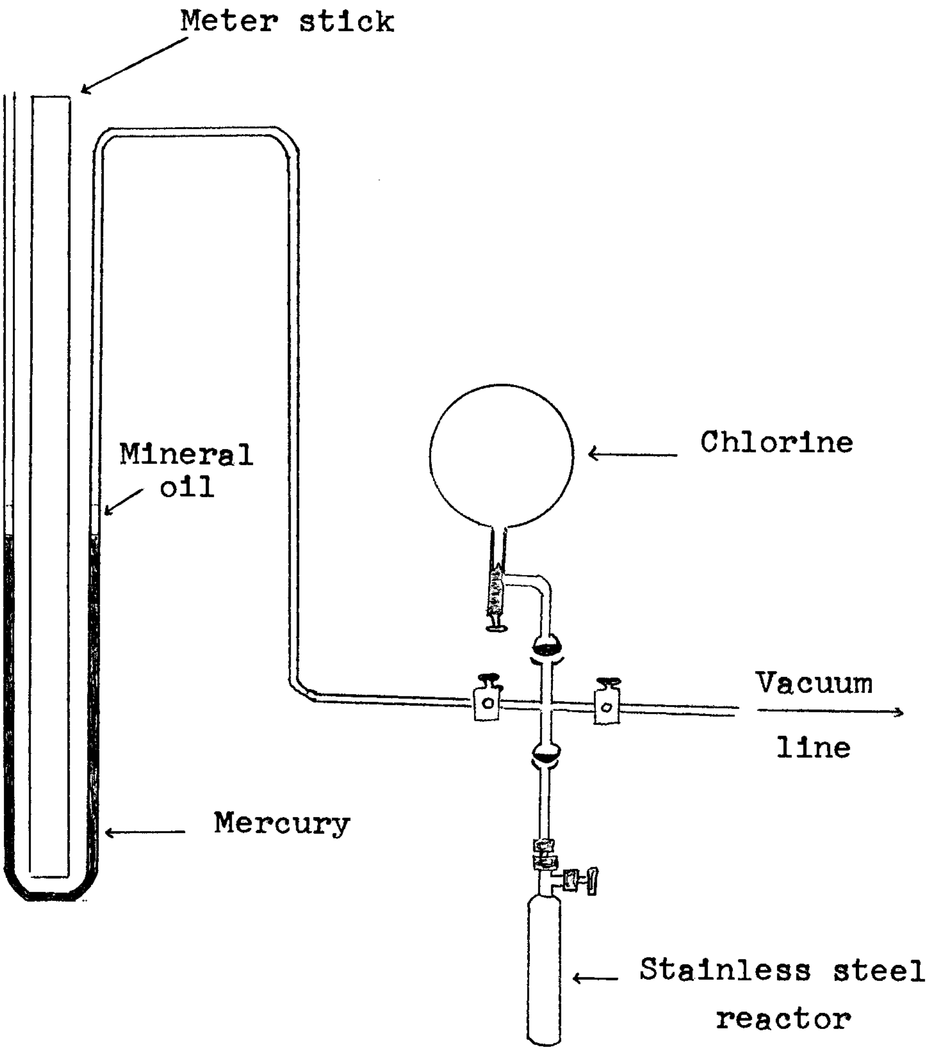
and Siegel.[33] Ten gm (0.092 mole) $(CH_3)_4NCl$ was converted to the hydroxide by passage through an anion exchange column. The aqueous solution was evaporated to a syrup and dissolved in methanol. A stoichiometric amount of HF was added and the resulting solution again evaporated to a syrup and taken up in methanol. The resulting solution was evaporated to dryness and heated to 100°C at 2-3 mm Hg for two hours yielding a white solid. The white solid was recrystallized from isopropanol. A sample of the recrystallized material was taken for fluoride analysis (calculated 20.46% found 17.67%).

VIII. Reaction of $C_6H_5SF_3$, CsF and Cl_2 in Stainless Steel

7.3610 grams (0.0485 mole) of cesium fluoride was added to the metal reactor (Figure 10) and evacuated to 10^{-4} mm Hg at 200°C to remove all traces of water.[78] 11.0778 gm (0.0667 mole) of freshly distilled "$C_6H_5SF_3$" was then added to the reactor in a nitrogen filled enclosure. A small portion of chlorine was condensed into the reactor at -78°C, the valve closed and the reactor warmed to 60°C (Figure 10). This process was repeated until 1.04 gm (0.0297 mole) of chlorine had been absorbed and repeated condensations resulted in no further absorption. The reaction mixture was vacuum distilled yielding a colorless liquid identified by infrared spectral analysis as $C_6H_5SF_3$.

IX. Reaction of $C_6H_5SF_3$, CsF and Cl_2 in Stainless Steel

FIGURE 10
STAINLESS STEEL REACTOR
CHLORINATION APPARATUS



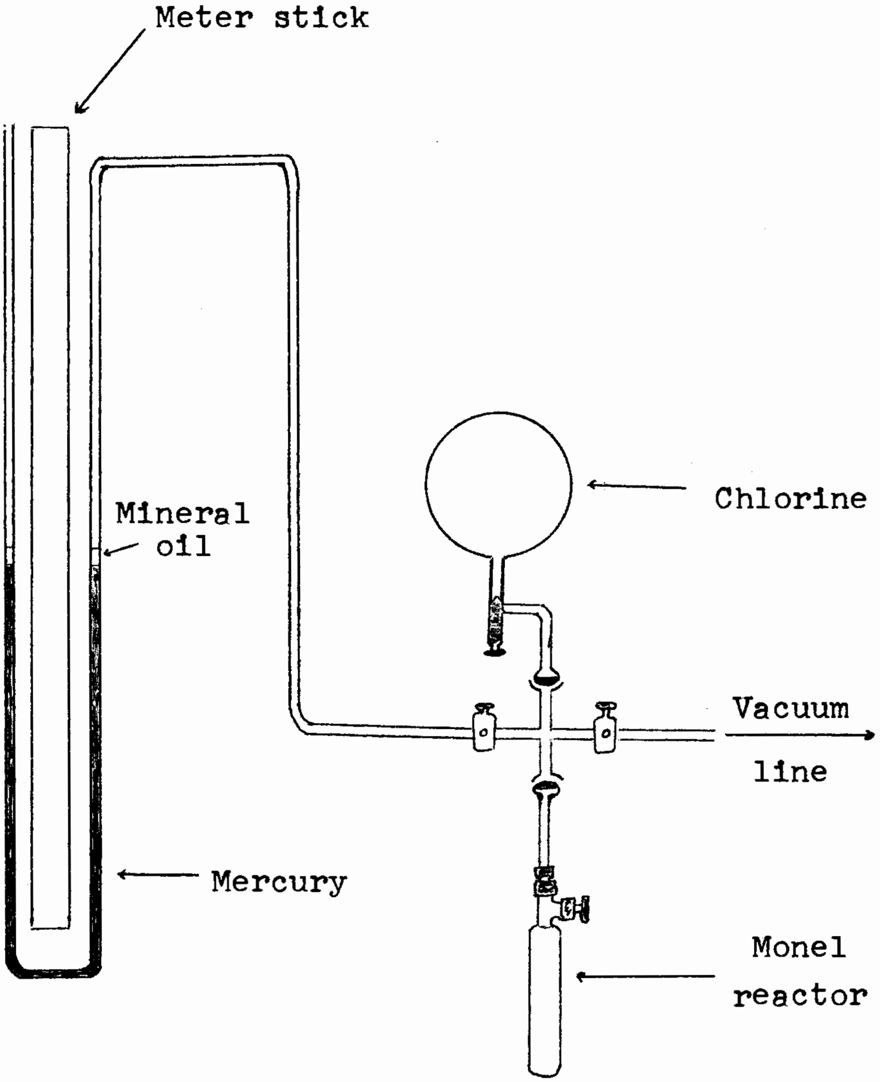
The above reaction was repeated at 170°C using 7.0824 gm (0.0426 mole) of $C_6H_5SF_3$ and 4.5812 gm (0.0301 mole) of cesium fluoride. The reaction vessel and cesium fluoride were pre-chlorinated at 170°C to minimize absorption due to the reactor and cesium fluoride. After repeated condensations and heatings the reactor was found to absorb 0.532 gm (0.0153 mole) of chlorine. The vessel was opened in a nitrogen filled enclosure. The residue observed consisted of a transparent amber colored solid and a dark brown residue. The amber solid was fused with sodium metal. Qualitative analysis of the solid indicated sulfide, fluoride and chloride ions. A sample was quantitatively analyzed by Schwarzkopf Microanalytical Laboratory and found to contain 22.15% sulfur, 49.37% carbon and 2.60% hydrogen. Quantitative analysis of the fused solid for fluorine and chlorine resulted in non-reproducible values for the remaining 25.88%.

X. Reaction of $C_6H_5SF_3$, CsF and Cl_2 in Monel

A monel reactor (Figure 11) was charged with 7.0038 gm (0.0435 mole) of "$C_6H_5SF_3$" and 5.1030 gm of dried cesium fluoride. The mixture was heated to 220°C for two days. A liquid sample was removed and proved to be $C_6H_5SF_3$ by infrared spectral analysis. Another sample (0.2983 gm) of the substance corresponding to $C_6H_5SF_3$ was removed, hydrolyzed and titrated for fluoride (calc. 34.5% F^-, before heating

FIGURE 11

MONEL CHLORINATION APPARATUS



24.8% F^-, after heating 24.2% F^-). The cylinder was returned to the vacuum line, evacuated, 1.2567 gm (0.0354 mole) of chlorine condensed into the cylinder and the reactor heated to 220°C for four days. The valve was opened and a pressure increase observed on a mercury manometer. The increase was due to the escape of 6.2 mmoles of gas from the reactor. The bulb (see Figure 11) was then isolated and mercury introduced to remove all remaining chlorine. A mass spectrum of the residual gas was taken (Table X) and identified as the hydrolysis products of SF_4.

TABLE X

MASS SPECTRUM OF RESIDUAL GAS (70 V)

m/e	Assigned Species	Intensity relative to SOF^+
48	SO^+	0.600
64	SO_2^+	0.800
67	SOF^+	1.000
86	SOF_2^+	0.460

A liquid (3.00 gm) was vacuum transferred from the monel reactor. The liquid was separated by distillation into two colorless fractions. These fractions were identified via infrared and mass spectra as $C_6H_5SO_2F$ (Figure 8, Table IX) and C_6H_5Cl (Figure 12, Table XI). The major part of the distillate was C_6H_5Cl.

TABLE XI

MASS SPECTRUM OF C_6H_5Cl (70 V)

m/e	Assigned Species	Intensity relative to $C_6H_5^+$
39	$C_3H_3^+$	0.222
50	$C_4H_2^+$	0.333
51	$C_4H_3^+$	0.396
56	$C_6H_5Cl^{++}$	0.124
77	$C_6H_5^+$	1.000
112	$C_6H_5Cl_{35}^+$	0.902
114	$C_6H_5Cl_{37}^+$	0.288

A remaining non-volatile liquid that could not be vacuum transferred at room temperature was mechanically removed from the cylinder and distilled at 152-157°C at 0.6 mm Hg. Infrared (Figure 13) and mass (Table XII) spectra of this material were taken. Qualitative analyses after sample fusion indicated the sample contained carbon, sulfur, fluorine and chlorine. Quantitative analyses indicated the material contained 34.85% F^- and 14.65% Cl^-. Cyroscopic molecular

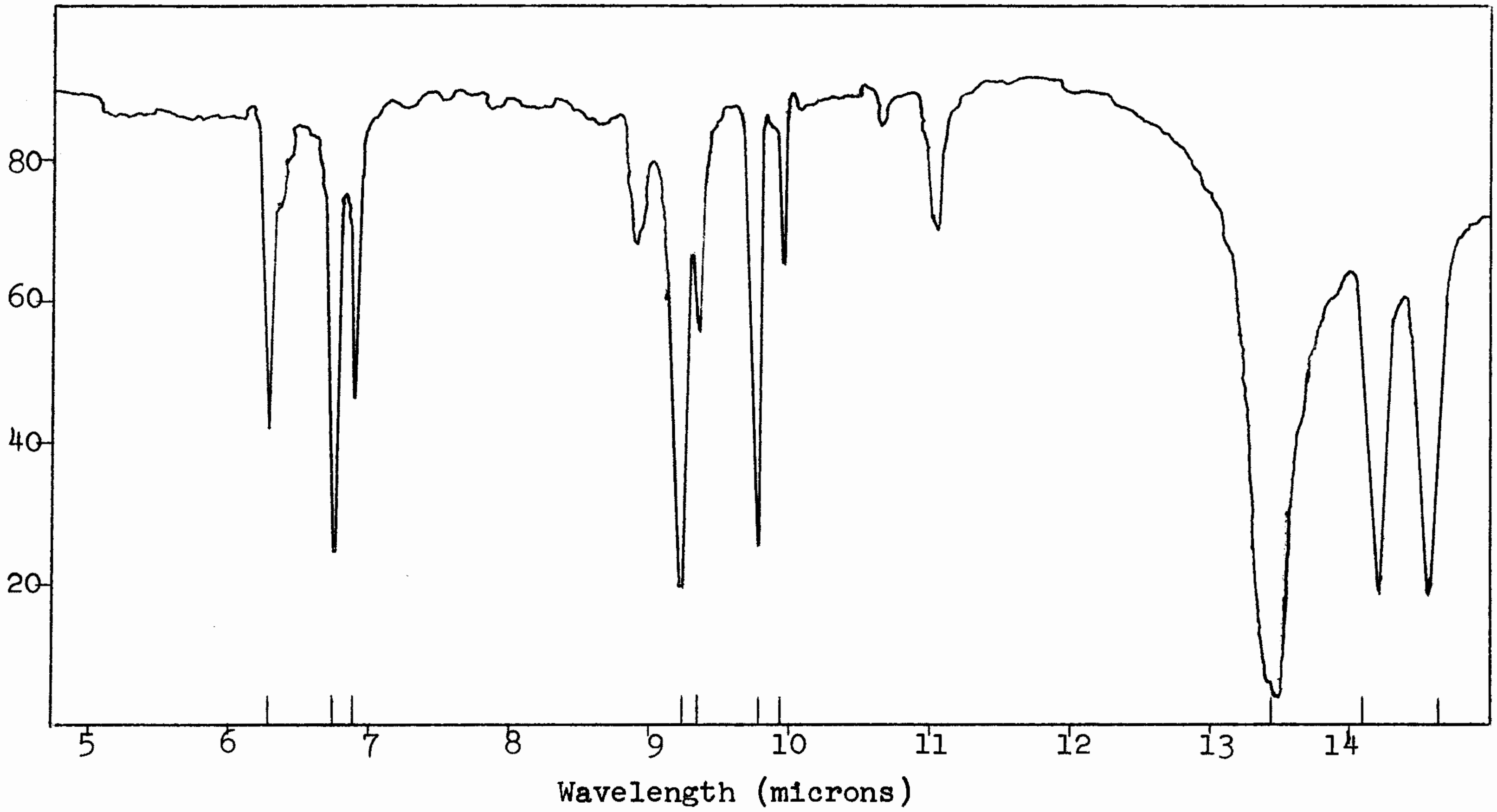


FIGURE 12

INFRARED SPECTRUM OF C_6H_5Cl

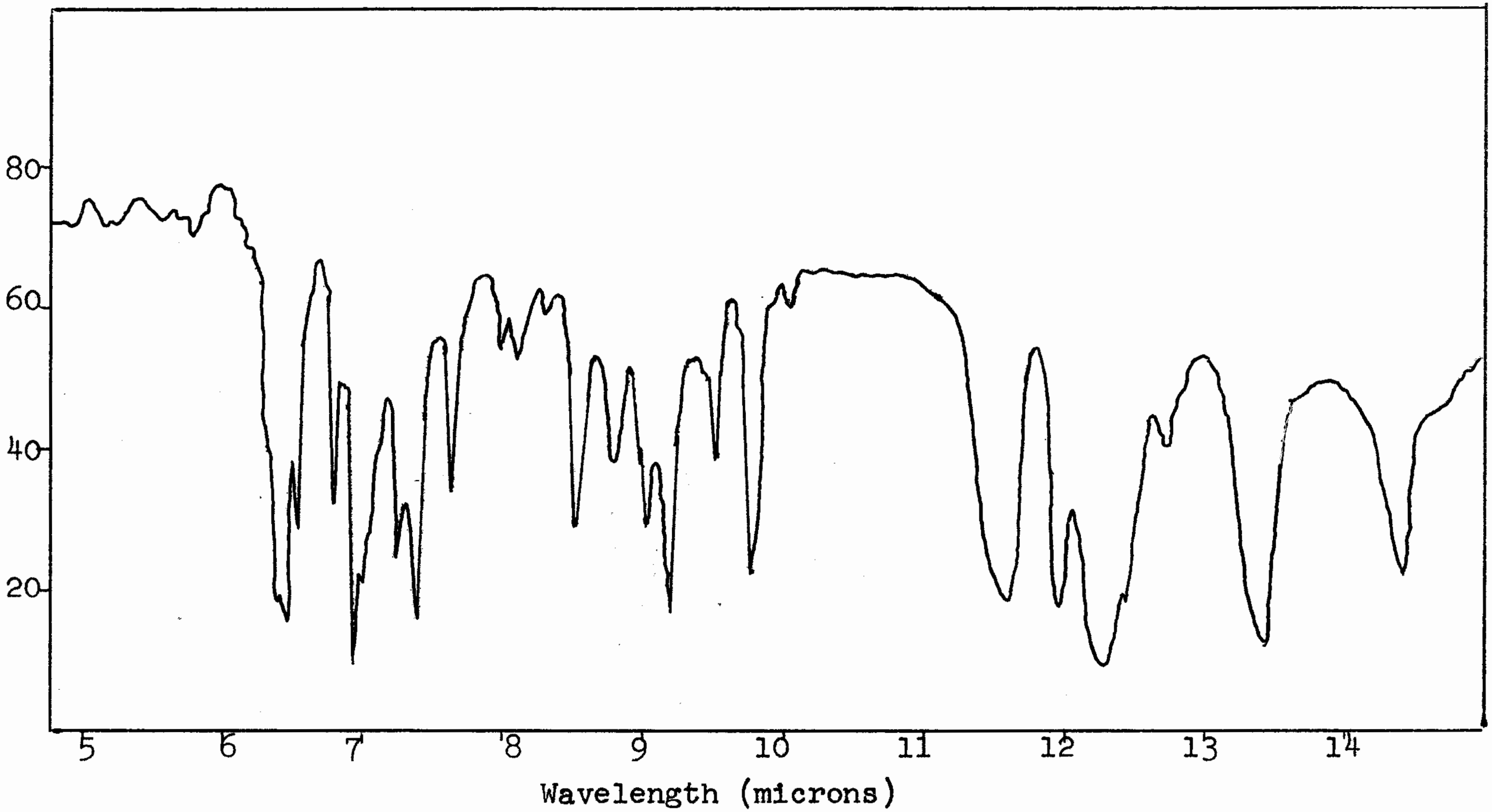


FIGURE 13

INFRARED SPECTRUM OF MIXTURE CONTAINING $C_6H_5SF_4Cl$, $FC_6H_4SF_4Cl$ AND $ClC_6H_4SF_4Cl$

weight determinations in benzene yielded a molecular weight of 233 g/mole. The analytical data support the proposition that the material was a mixture of $C_6H_5SF_4Cl$ (M.W. 219.9746, % F = 34.5, % Cl = 15.9); $ClC_6H_4SF_4Cl$ (M.W.254.064, % F = 29.6, % Cl = 27.2); and $FC_6H_4SF_4Cl$ (M.W. 238.056, % F = 39.5, % Cl = 14.7).

TABLE XII

MASS SPECTRUM* OF NON-VOLATILE LIQUID

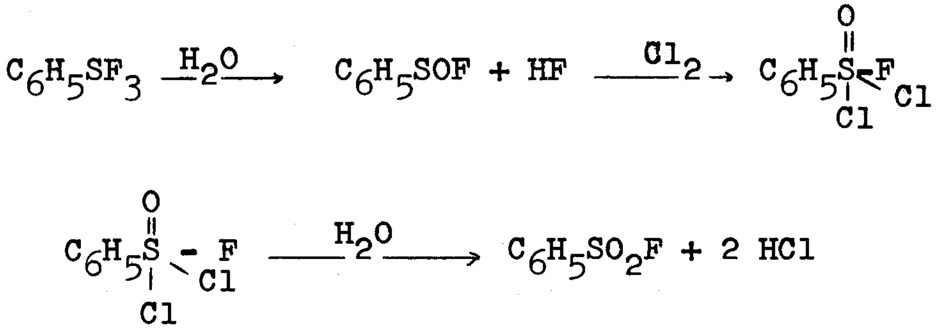
m/e reported	m/e calc.	Assigned Species	Intensity relative to $C_6H_5SF_3^+$
255 ±1	254	$ClC_6H_4SF_4Cl^+$	0.532
239 ±1	238	$FC_6H_4SF_4Cl^+$	0.403
219.9652	219.9746	$C_6H_5SF_4Cl^+$	0.565
187 ±1	187	Unassigned	0.258
185 ±1	185	$C_6H_5SF_4^+$	0.806
183 ±1	183	Unassigned	0.855
166 ±1	166	$C_6H_5SF_3^+$	1.000

*This is only a portion of the mass spectrum run on the MS 9 high resolution mass spectrometer.

DISCUSSION

To date, no di-substituted derivatives of SF_6 have been prepared containing a S-Cl bond. Such species, if prepared would be of structural interest and would be useful synthetic intermediates. The specific problem chosen was the synthesis of the SF_5Cl analog, $C_6H_5SF_4Cl$. SF_5Cl is best prepared by the reaction of SF_4, CsF and Cl_2.[32] Since reported chemistry of $C_6H_5SF_3$ parallels that of SF_4, the suggested route to $C_6H_5SF_4Cl$ was through the direct interaction of $C_6H_5SF_3$, CsF and Cl_2. The proposed reaction was studied under a variety of conditions. The attempted syntheses run in pyrex glass and teflon (Reactions IV-VI) resulted in the formation of benzenesulfonyl fluoride, $C_6H_5SO_2F$. Suggested routes for the formation of $C_6H_5SO_2F$ are:

(1)



$$C_6H_5SF_3 \xrightarrow{H_2O} C_6H_5SOF + HF \xrightarrow{Cl_2} C_6H_5\overset{O}{\underset{Cl}{S}}\begin{smallmatrix}F\\ Cl\end{smallmatrix}$$

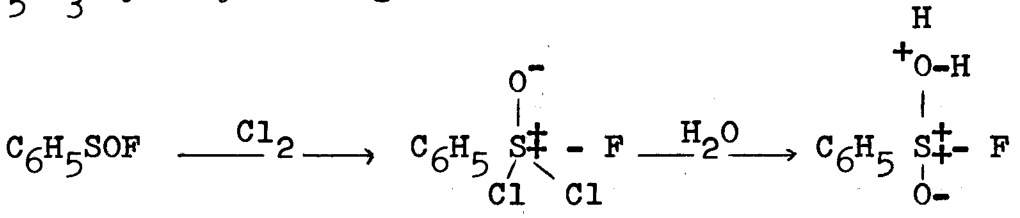
$$C_6H_5\overset{O}{\underset{Cl}{S}}\begin{smallmatrix}-F\\ Cl\end{smallmatrix} \xrightarrow{H_2O} C_6H_5SO_2F + 2\ HCl$$

(2) $C_6H_5SF_3 \xrightarrow{Cl_2} C_6H_5SF_3Cl_2 \xrightarrow[\text{or } H_2O]{SiO_2} C_6H_5SO_2F + 2HCl + 2HF$

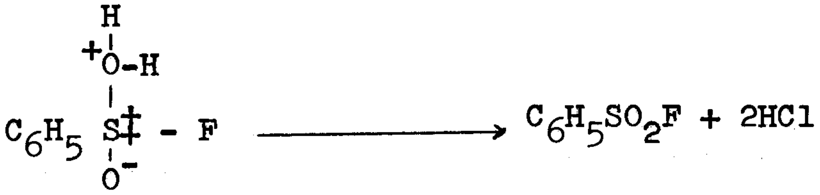
$$(3)\quad C_6H_5SF_3 + F^- + Cl_2 \longrightarrow C_6H_5SF_4Cl + Cl^-$$

$$C_6H_5SF_4Cl + Cl^- \xrightarrow[\text{or } H_2O]{SiO_2} C_6H_5SO_2F + Cl^- + F^-$$

Route (3) is the least probable since $C_6H_5SF_4Cl$ has since been prepared and seems to be stable to hydrolysis. Formation of $C_6H_5SO_2F$ by route (2) suggests the presence of $C_6H_5SF_3Cl_2$ either as an intermediate or as an activated complex. If $C_6H_5SF_3Cl_2$ is formed, it is feasible that it could be instantly hydrolyzed to $C_6H_5SO_2F$ since compounds containing S-Cl bonds are known to be quite hydrolytically reactive.[1, 80] The suggested reaction route in equation (1) presents the most favorable situation. C_6H_5SOF is a known product of the hydrolysis of $C_6H_5SF_3$.[37] A proposed mechanism similar to the hydrolysis of $C_6H_5SCl_3$ in the presence of chlorine[80] seems feasible. The proposed mechanism as applied to $C_6H_5SF_3$ hydrolysis is given below.



$$C_6H_5SOF \xrightarrow{Cl_2} C_6H_5\,\overset{O^-}{\underset{Cl\quad Cl}{S^{\ddagger}}} - F \xrightarrow{H_2O} C_6H_5\,\overset{\overset{H}{{}^+O-H}}{\underset{O-}{S^{\ddagger}}} - F$$



$$C_6H_5\,\overset{\overset{H}{{}^+O-H}}{\underset{O^-}{S^{\ddagger}}} - F \longrightarrow C_6H_5SO_2F + 2HCl$$

Assuming this route is correct, then the chlorination of C_6H_5SOF must occur rapidly since C_6H_5SOF is readily hydrolyzed to $C_6H_5SO_2H$.[37]

$$C_6H_5SOF + H_2O \longrightarrow C_6H_5SO_2H + HF$$

Precautions were taken to avoid introduction of moisture in the system (Figures 7 and 9). All mechanical transfers were made in a polyethylene enclosure, however, the cesium fluoride was not predried before use. A sample of the undried CsF was titrated for fluoride (reported 12.51%, found 12.28% F^-). Assuming water as the only impurity, the water was present in a 1:10 mole ratio with CsF. Further, any route to the preparation of $C_6H_5SO_2F$ in the preceding reactions without chlorine may be disregarded. $C_6H_5SF_3$ was distilled directly into a receiver containing undried cesium fluoride with no evidence of $C_6H_5SO_2F$ formation (Reaction VI).

The hydrolysis in the preceding reactions was assumed to occur because of the water introduced with the cesium fluoride. Hence, cesium fluoride was dried by heating to 200°C at 10^{-4} mm Hg in the remaining reactions.[78] Chlorination of a mixture of 0.0485 mole dried cesium fluoride and 0.0667 mole "$C_6H_5SF_3$" at 60°C in a 303 stainless steel reactor yielded a colorless liquid identified by infrared spectral analysis as $C_6H_5SF_3$. Although no change in the reactants was observed, the vessel absorbed 1.04 gm (0.0297 mole) of chlorine. It was assumed that the chlorine absorption was due to reaction with the cylinder. The procedure was modified and repeated. The dried CsF (0.0301 mole) and cylinder were pre-chlorinated at 170°C. "$C_6H_5SF_3$" (0.0426 mole) was added and the mixture found to absorb 0.532 gm (0.0153 mole) of chlorine at 170°C. After reaction, a mixture consisting of a transparent amber solid and a dark brown granular solid was observed in the reactor. The amber solid was analyzed by Schwarzkopf Microanalytical Laboratories and reported to contain 22.15% sulfur, 49.37% carbon and 2.6% hydrogen. Several samples of this solid were fused for quantitative measurements of fluoride and chloride. No reproducible values were obtained. If only fluorine was considered present, in addition to the C, H and S reported by Schwarzkopf, the empirical formula would be $C_{5.95}H_{3.71}S_{1.00}F_{1.97}$. A number of structures may be proposed that qualitatively agree with this formula. Some speculations concerning the nature of this material follow.

The analyzed hydrogen percentage does not allow enough error for one to assign a F-C_6H_4SF type structure. A proposed structure of the type illustrated in (Figure 14) as a segment of a polymer would have an empirical formula of $C_6H_{3.67}SF_2$ and analyze 49.43% carbon, 21.97% sulfur, 2.52% hydrogen and 26.08% fluorine. It is feasible that trisubstitution of rings 2 and 3 would not occur due to steric hindrances. (The benzene rings would be expected to occupy

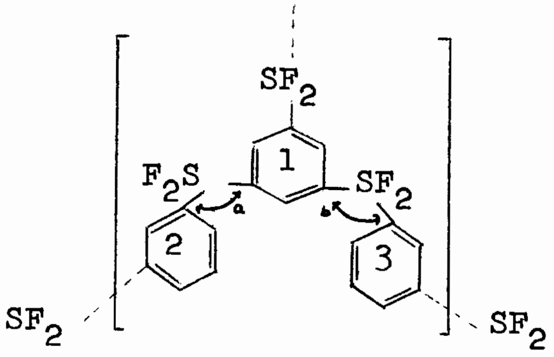
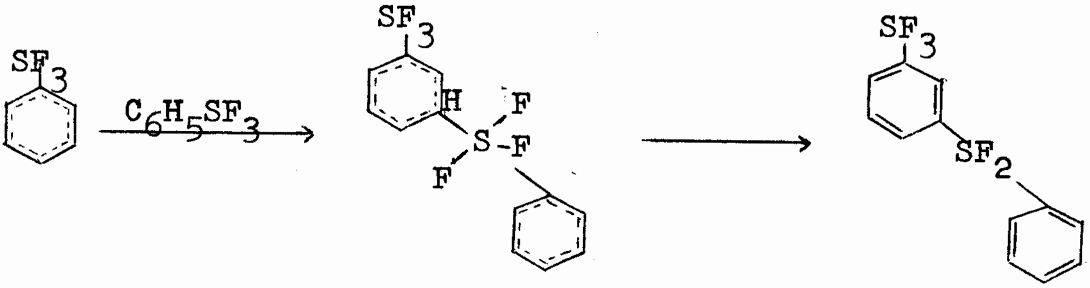


FIGURE 14

PROPOSED STRUCTURE FOR $C_6H_{3.67}SF_2$

the equatorial positions in the tetravalent sulfur,[10] thus making angles a and b near 120°. The fusion of the molecule in polymeric form would require that the benzene rings lie in a plane. If the rings were planar and angles a and b near 120°, substitution on the second meta-position would be sterically hindered). A proposed mechanism would be a direct attack at the meta-position by a neighboring sulfur atom.



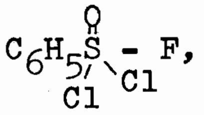
Since the chlorine attacked the cylinder the reaction may proceed as proposed in the presence of a Lewis acid, (ie. $FeCl_3$).

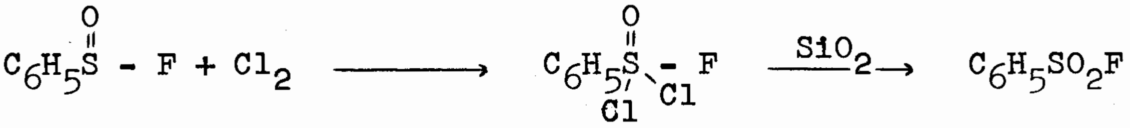
The reaction was repeated in a 95 ml monel reactor using 0.0435 mole of "$C_6H_5SF_3$", 0.0355 mole of dried cesium fluoride and 0.0354 mole of chlorine at 220°C for four days. The reactor was opened and 6.2 mmoles of gas was measured. After removal of chlorine by the introduction of mercury a mass spectrum was run on the residual gas. The spectrum indicated the presence of SO_2^+, SO^+, SOF^+ and SOF_2^+. Species of this type indicate the hydrolysis of SF_4 (Equations 4, 5 and 6).

$$(4) \quad SF_4 + H_2O \longrightarrow SOF_2 + 2HF$$

$$(5) \quad SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$(6) \quad H_2O + SOF_2 \longrightarrow SO_2 + 2HF$$

A mixture of two volatile liquids was vacuum transferred from the reactor and redistilled. The major portion of the redistilled material was identified by mass and infrared spectra (Table XI, Figure 12) as chlorobenzene. The second liquid was identified as benzenesulfonyl fluoride (Table IX, Figure 8). Since C_6H_5SOF is known to be a contaminant in the $C_6H_5SF_3$ used, the formation of $C_6H_5SO_2F$ could result from chlorination of C_6H_5SOF producing a species,  $C_6H_5\overset{O}{\underset{Cl\ \ Cl}{S}}-F$, which would be readily hydrolyzed to $C_6H_5SO_2F$ in the vacuum transfer process.



$$C_6H_5\overset{\overset{O}{\|}}{S}-F + Cl_2 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{\underset{Cl\ \ Cl}{S}}-F \xrightarrow{SiO_2} C_6H_5SO_2F$$

The remaining non-volatile liquid was mechanically transferred to a glass distillation apparatus where it was vacuum distilled at 150-157°C at 0.6 mm Hg. Mass spectral analysis indicates the liquid was a mixture containing the desired $C_6H_5SF_4Cl$, $F-C_6H_4SF_4Cl$ and $Cl-C_6H_4SF_4Cl$. A molecular weight (233 g/mole) was indicated by freezing point depression. Infrared spectral analysis leads one to assume that the mixture consists predominately of a mono-substituted moiety. The overtone region ($5-6\mu$) shows four distinct peaks, although not well resolved, indicative of mono-substitution. The C-H out-of-plane bending bands are also consistent with mono-substitution. A mono-substituted benzene absorbs at 770-730 cm^{-1} and 710-690 cm^{-1} corresponding to the 736 cm^{-1} and 685 cm^{-1} observed for the mixture. Bands present at 858 cm^{-1} and 808 cm^{-1} may be assigned to the S-F stretches of sulfur VI fluorides.[37, 56]

The existence of SF_4 and chlorobenzene in the system may be explained by the thermal decomposition of $C_6H_5SF_4Cl$. Sheppard[56] postulated the thermal decomposition of $C_6H_5SF_5$ as yielding C_6H_5F and SF_4.

$$C_6H_5SF_5 \longrightarrow C_6H_5F + SF_4$$

By an analogous type of decomposition, $C_6H_5SF_4Cl$ may be expected to yield C_6H_5Cl and SF_4. The formation of $C_6H_5SF_4Cl$ is assumed to occur through a route similar to that postulated for SF_5Cl formation in the presence of CsF.

$$C_6H_5SF_3 + CsF \longrightarrow Cs^+C_6H_5SF_4^- \xrightarrow{Cl_2} C_6H_5SF_4Cl + CsCl$$

The stability of the $Cs^+C_6H_5SF_4^-$ is not established. However, use of a larger cation such as $(CH_3)_4NF$ may stabilize the complex enough to allow isolation of the corresponding salt.

Further study of this system would include repetition of the synthetic procedures, separation of the desired product, $C_6H_5SF_4Cl$ from its substituted derivatives and study of the physical and chemical properties of $C_6H_5SF_4Cl$.

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