# NITROGEN–SULFUR–FLUORINE IONS

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## I. Introduction

Although the chemistry of nitrogen–sulfur–fluorine compounds was fully discussed in a recent article (*58*), the rapid development of this field renders a new review timely, especially as a fresh approach is adopted. Summaries of work on sulfur–nitrogen anions were published some time ago (*12, 13*). The literature that has been covered earlier (*58*) will be dealt with briefly here insofar as it is necessary for the general cohesion of this article, but the main emphasis is placed on more recent work.

The chemistry of nitrogen–sulfur–fluorine compounds is in the main concerned with covalent substances, the end products being also mostly covalent, but intermediates are often ionic in character. In this article it is planned to show which ions have been prepared and which are in general possible, and also to put this wide range of possibilities on a systematic basis. Known reactions are examined to determine if they occur through ionic intermediates and how these fit into the reaction scheme. In this connection, ways may sometimes be found to trap these ions. Nitrogen–sulfur–fluorine ions are defined primarily as compounds containing these elements, but derivatives that can be prepared from N—S—F compounds (e.g., $NS^+$) will also be considered. Insofar as it is necessary to secure an overall picture, related compounds will also be discussed (e.g., pure SF ions or perfluoroalkyl derivatives) although the selection of literature in this connection is somewhat arbitrary. The chemistry of N—S—F ions is still almost in its infancy. Whereas much information is available on anions, especially for tetracoordinated compounds of S(VI), little is known about the cations. This paucity of information does, however, enable us to recognize what possibilities there are, particularly for new syntheses.

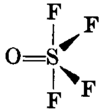
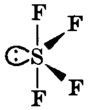
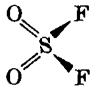
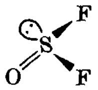
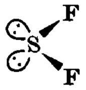
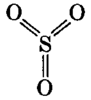
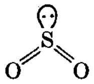
## II. Classification of Sulfur Compounds According to Their Coordination Numbers

Sulfur is one of the most interesting of the chemical elements because it occurs with such different valencies and coordination numbers and is able to form bonds varying in type from formal single bonds to triple bonds. In addition, it readily enters into the formation of chains and rings as, for example, in sulfur–nitrogen chemistry.

It is difficult to deal with this versatility, but the problem may be simplified by classifying sulfur compounds according to their coordination numbers. Structural investigations available so far show the free electron pair in sulfur compounds to be sterically active, and treatment of these molecules in terms of the Gillespie and Nyholm rules (*48*) is completely justified. Table I shows the various coordination possibilities in sulfur fluorides and oxyfluorides.

Sulfur (VI) has no free pair of electrons, and coordination numbers of 6, 5, 4, and 3 are found. Four-valent sulfur can reach a maximum coordination number of 5, the position of the doubly bonded oxygen in $OSF_4$ being taken in ⊂$SF_4$ by a free pair of electrons. Two doubly bonded oxygens and singly bonded fluorine atoms lead to tetrahedral coordination of S(VI) in $SO_2F_2$, the corresponding compound in the S(IV) system being ⊂$SOF_2$, whereas in  $F\overset{\subset}{\underset{\subset}{S}}F$ the last oxygen is also replaced by a free pair of electrons. As in the transition from $OSF_4$ to ⊂$SF_4$, a corresponding gradation in chemical behavior in the series $SO_2F_2$—⊂$SOF_2$— $\overset{\subset}{\underset{\subset}{S}}F_2$ is found. The relationship between isocoordinated compounds with different oxidation states is essentially greater than that between differently coordinated representatives of the same oxidation state.

TABLE I
Coordination Numbers in Neutral Sulfur Fluorides, Oxyfluorides, and Oxides

| Coordination No. | S(VI) | S(IV) | S(II) |
|---|---|---|---|
| 6 |  | — | — |
| 5 |  |  | — |
| 4 |  |  |  |
| 3 |  |  |  |

Variation in coordination number is fairly restricted in sulfur ions and for S(VI) the anionic and cationic species encountered are almost exclusively tetra- or hexacoordinated. The same is true in the main for sulfur(IV), although here cations with lower coordination are possible.

## III. Acyclic Nitrogen–Sulfur–Fluorine Anions

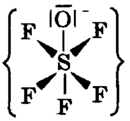
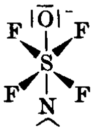
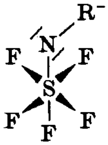
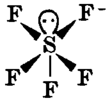
The negative charge is carried by nitrogen in nitrogen–sulfur–fluorine anions, whereas in cations the positive charge may be assigned to sulfur. As a result, the chemistry of the anions is more that of the nitrogen atom, whereas for the cations reactions occur at the central sulfur atom. Exceptions are the sulfur–fluorine anion $\odot SF_5^-$ and, perhaps, also $\overset{\odot}{F}SO_2^-$, for which attempts to transfer the species intact in ionic reactions result in decomposition to $F^-$ and $SF_4$ or $SO_2$.

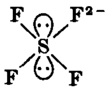
### A. Hexacoordinated Anions

Hexacoordinated anions have been known for a long time in the chemistry of both sulfur(VI) and sulfur(IV) through the species $OSF_5^-$ (*135*) and $\odot SF_5^-$ (*154*). The corresponding compound of bivalent sulfur,

TABLE II

Possible Hexacoordinated Nitrogen–Sulfur–Fluorine Anions

| | | | |
|---|---|---|---|
| S(VI) |  |  |  |
| S(IV) |  |  | — |



cannot be prepared both because of the great instability of $SF_2$ (*141*) and because addition of 2 fluoride ions to tetrahedrally coordinated $\overset{..}{\underset{..}{S}}F_2$ is thermodynamically unfavorable. No examples are known in sulfur chemistry in which it has been possible to add fluoride ions to a neutral tetrahedral molecule and form a stable anion. Thus there remain in nitrogen–sulfur–fluorine chemistry only the possibilities shown in Table II. It is theoretically possible in $OSF_5^-$ or in $:SF_5^-$ to replace an atom of fluorine by an amino group or, in the case of S(VI), to introduce in place of $|\overline{\underline{O}}^-$— the isosteric $R\overline{\underline{N}}^-$— group.

### 1. *Pentafluorosulfuroxy Anion,* $SF_5O^-$, *and Its Derivatives*

The $OSF_5^-$ ion has been assumed to be an intermediate in the catalytic fluorination of $OSF_4$ to $SF_5OF$ (*39*, *40*, *135*) and the cesium salt may be prepared at room temperature in $CH_3CN$ (*90*) or at elevated temperature without a solvent (*135*, *23*):

$$OSF_4 + CsF \xrightarrow[RT]{CH_3CN} Cs^+\ OSF_5^- \tag{1}$$

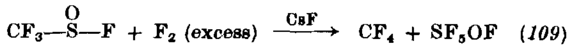
The salt is stable at room temperature, but $OSF_4$ is evolved almost quantitatively at higher temperatures. One fluorine atom in sulfuroxy tetrafluoride may be replaced by an amino or phenoxy group (*53*, *159*, *160*, *161*, *131*), and it has also proved possible to replace 2 fluorine atoms by phenoxy- or perfluoroalkyl groups. As for $OSF_5^-$, these derivatives should also yield hexacoordinated anions. It would, however, be expected that replacement of fluorine atoms by bulky and less electronegative groups would reduce the ability of the central sulfur atom to accept fluoride ions, and it is, in fact, found that dialkylaminosulfur oxytrifluoride is unable to add fluoride ions (*94*):

$$(CH_3)_2NSOF_3 + CsF \xrightarrow[RT]{CH_3CN} \textit{no stable salt formed} \qquad (2)$$

Few reactions have so far been carried out with $OSF_5^-$. Compound $SF_5OF$ is formed with fluorine (*135*), and $SF_5OCl$ can be isolated following decomposition of the salt with FCl (*140*):

$$Cs^+\ SF_5O^- + FX \longrightarrow SF_5OX + CsF \qquad (X = F, Cl) \qquad (3)$$

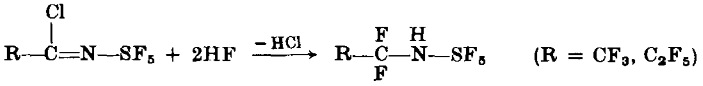
It has not so far proved possible to transfer the $OSF_5^-$ ion to other systems by means of the cesium salt: Decomposition of the ion to $F^-$ and $OSF_4$ occurs. Reactions analogous to those shown in Eq. (3) are hardly to be expected with derivatives of the type $\{R—SOF_3\}$ as they would involve cleavage of the S—R bond, e.g.,



$$CF_3—\overset{O}{S}—F + F_2\ (\text{excess}) \xrightarrow{CsF} CF_4 + SF_5OF \quad (\mathit{109}) \qquad (4)$$

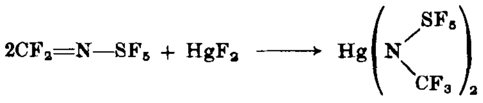
## 2. *Pentafluorosulfanylamide Anions*, $SF_5—\underline{\bar{N}}—R^-$

*a. Derivatives with Perfluoroalkyl Groups.* Acids containing these anions may be prepared from perhaloazomethines and HF (*154*):



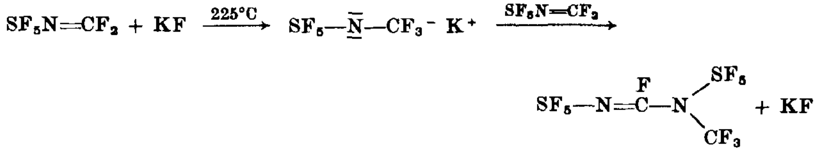
$$R—\overset{\overset{Cl}{|}}{C}{=}N—SF_5 + 2HF \xrightarrow{-HCl} R—\underset{F}{\overset{F}{C}}—\overset{H}{N}—SF_5 \qquad (R = CF_3, C_2F_5) \qquad (5)$$

The mercury derivative is produced from $HgF_2$ and the corresponding perfluorinated azomethine (*154*):



(6)

Alkali metal derivatives have not actually been described, although the formation of dimers on heating the azomethine with KF shows that they must be formed as intermediates (*154*):

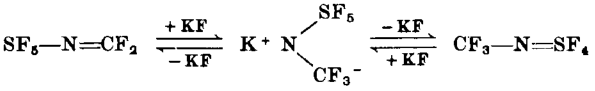


(7)

Partial isomerization is also observed in this reaction,

$$SF_5N{=}CF_2 \xrightarrow{\sim} F_4S{=}N{-}CF_3 \qquad (8)$$

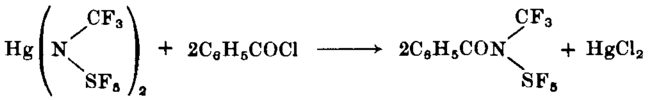
This too may be satisfactorily explained by assuming the formation of an ionic intermediate:



$$SF_5{-}N{=}CF_2 \underset{-KF}{\overset{+KF}{\rightleftharpoons}} K^+\,N(SF_5)(CF_3)^- \underset{+KF}{\overset{-KF}{\rightleftharpoons}} CF_3{-}N{=}SF_4 \qquad (9)$$

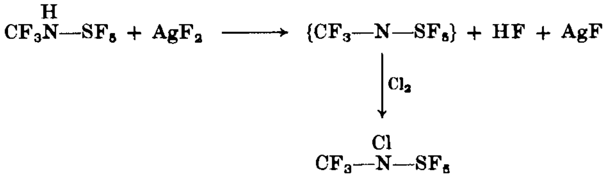
Equilibrium (9) has not been investigated, but, in purely qualitative terms, it follows from these observations that $F^-$ addition occurs more readily to the C=N— than to the S=N— double bond.

The mercury compound reacts with active halides (*154*), e.g.,



$$Hg\left(N\begin{matrix}CF_3\\SF_5\end{matrix}\right)_2 + 2C_6H_5COCl \longrightarrow 2C_6H_5CON\begin{matrix}CF_3\\SF_5\end{matrix} + HgCl_2 \qquad (10)$$

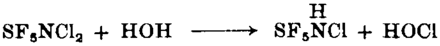
The preparation of the corresponding N—Cl compound presumably occurs by a radical mechanism:



$$CF_3\overset{H}{N}{-}SF_5 + AgF_2 \longrightarrow \{CF_3{-}N{-}SF_5\} + HF + AgF \xrightarrow{Cl_2} CF_3{-}\overset{Cl}{N}{-}SF_5 \qquad (11)$$

*b. Derivatives with Inorganic Groups.* If a proton in pentafluorosulfanylamine, $SF_5NH_2$, is replaced by an inorganic group rather than a perfluoroalkyl group, the resulting compound will naturally possess acid character. Compounds of this type mentioned in the literature include the following:

i. *N*-Chloropentafluorosulfanylamine (*28*),



$$SF_5NCl_2 + HOH \longrightarrow SF_5\overset{H}{N}Cl + HOCl \qquad (12)$$

No information on this compound is available apart from its mass spectrometric identification.

ii. *N*-Fluorosulfonylpentafluorosulfanylamine (*73*),

$$F_5S{-}N{=}SOF_2 + H_2O \xrightarrow[-HCl]{(C_6H_5)_4AsCl} [F_5S{-}\overline{\underline{N}}{-}SO_2F]^-[(C_6H_5)_4As]^+ + HF \qquad (13)$$

It is obtained as the tetraphenylarsonium salt in quantitative yield by alkaline hydrolysis of $SF_5NSOF_2$. The hydrolysis mechanism will be considered in discussing the fluorosulfonylamine.

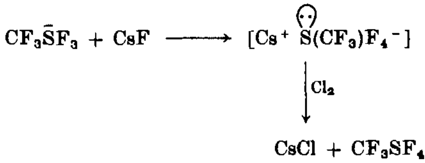
### 3. *The* $\odot SF_5^-$ *Ion and Its Derivatives*

Cesium fluoride reacts with $\bar{S}F_4$ as follows (*154*):

$$\odot SF_4 \text{ (excess)} + CsF \xrightarrow[250°C]{125°-} Cs^+ \ \odot SF_5^- \qquad (14)$$

Products obtained in this way are, however, heavily contaminated with CsF (*154*) and so far it has not been possible to prepare the compound in a pure state. Exact information on the stability of the salt is also lacking [the dissociation pressure is greater than 1 atm at 150°C (*154*)]. It is known that $(CH_3)_4N^+ \odot SF_5^-$, which is prepared by a reaction analogous to that shown in Eq. (14), has only a small $SF_4$ dissociation pressure at room temperature (*38*, *155*). Nuclear magnetic resonance studies have not been made, but the vibrational spectrum shows clearly that the central sulfur atom in the ion is octahedrally coordinated, the fluorine ligands forming a square pyramid (*22*, *38*, *154*).

Since the $\odot SF_5^-$ ion is only moderately stable, therefore stable derivatives of the type $R\overset{\odot}{S}F_4^-$ are hardly to be expected. The $SF_5^-$ ion is an intermediate in the preparation of $SF_5Cl$ (*154*). Compound $CF_3SF_4Cl$ is isolated in the reaction between $CF_3\bar{S}F_3$ and $Cl_2$ in presence of CsF (*34*) and this may be explained by postulating intermediate formation of $Cs^+ \ CF_3\overset{\odot}{S}F_4^-$:

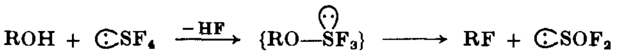


$$CF_3\bar{S}F_3 + CsF \longrightarrow [Cs^+ \ \overset{\odot}{S}(CF_3)F_4^-] \xrightarrow{Cl_2} CsCl + CF_3SF_4Cl \qquad (14a)$$

In the corresponding reaction with $(CH_3)_2N\bar{S}F_3$, only decomposition products, such as $SF_5Cl$, are found. This does not necessarily mean that the $(CH_3)_2N\bar{S}F_4^-$ ion has not been formed, although it is not very likely. Since $\odot SF_4$ adds fluoride ions less readily than $OSF_4$, a similar reaction path would be expected for the amino derivative.

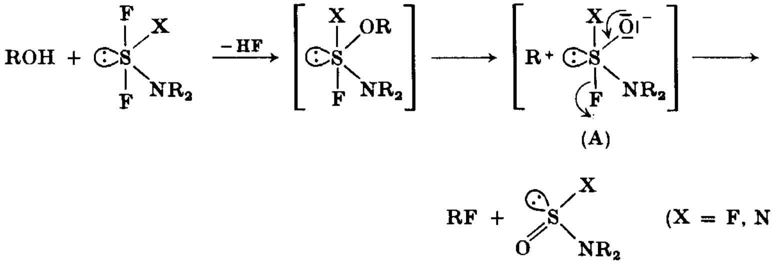
## B. Pentacoordinated Anions

As would be expected, pentacoordinated anions have not been isolated, since $F^-$ is split off and they go over to more stable tetracoordinated neutral compounds (*11*). Exchange of the OH group in alcohols for fluorine with the aid of $SF_4$ is a reaction of preparative significance (*70*):



$$ROH + \supset SF_4 \xrightarrow{-HF} \{RO\text{—}\overset{\frown}{S}F_3\} \longrightarrow RF + \supset SOF_2 \qquad (15)$$

Aminosulfur trifluorides or bisaminosulfur difluorides are more selective fluorinating agents (*100*):



(X = F, $NR_2$) (16)

The $R_2NSOF_2^-$ ion should be a better leaving group than $(R_2N)_2SOF^-$ and, as a result, the intermediate (A) has more ionic character in the first case. The stronger carbonium ion character of $R^+$ is established experimentally by the greater proportion of rearranged products. The solvent dependence of these reactions supports the mechanism given (*100*).

## C. TETRACOORDINATED ANIONS

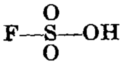
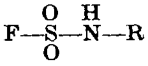
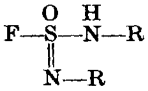
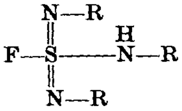
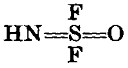
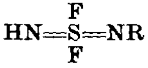
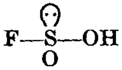
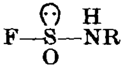
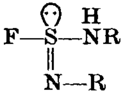
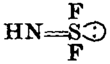
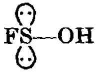
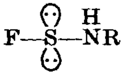
Table III shows the theoretical possibilities for tetracoordinated nitrogen–sulfur–fluorine anions. In discussing these numerous possibilities systematically we will take as our starting point the monobasic fluorooxy acids and the neutral oxyfluorides.

On paper we would expect the $OH^-$ groups in them to be replaceable by $\text{—}\underset{H}{\overline{N}}\text{—}R$ and the doubly bound oxygen by $R\overline{N}=$ or the isoelectronic $\underline{\overline{N}}^-=$ group. Although the possibilities for S(VI) are quite numerous, the free electron pair in S(IV) limits this variation very much, and for S(II) only a single possibility exists.

In Table III account has been taken of the fact that a singly bonded OH group adjacent to a doubly bonded nitrogen is unstable. Rearrangement always takes place to the energetically favored S═O—doubly bonded and —S—N— singly bonded system. A further rule

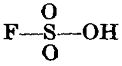
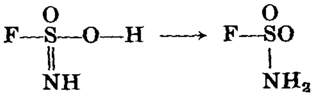
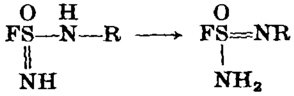
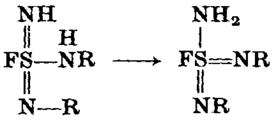
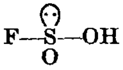
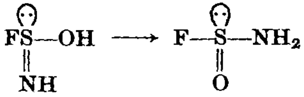
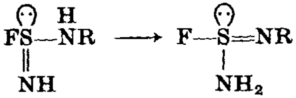
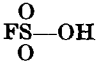
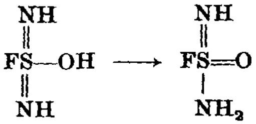
## TABLE III

### Tetrahedrally Coordinated Nitrogen–Sulfur–Fluorine Anions Derived from Fluorooxy Acids and Oxyfluorides

| Acid | Oxidation state | Parent acid | Nitrogen derivatives | | | Parent oxifluoride | Nitrogen derivatives | |
|---|---|---|---|---|---|---|---|---|
| Monobasic | VI |  $F{-}\overset{O}{\underset{O}{S}}{-}OH$ |  $F{-}\overset{O}{\underset{O}{S}}{-}\overset{H}{N}{-}R$ |  $F{-}\overset{O}{\underset{\underset{N-R}{\Vert}}{S}}{-}\overset{H}{N}{-}R$ |  $F{-}\overset{\overset{N-R}{\Vert}}{\underset{\underset{N-R}{\Vert}}{S}}{-}\overset{H}{N}{-}R$ | $OSF_2O$ |  $HN{=}\overset{F}{\underset{F}{S}}{=}O$ |  $HN{=}\overset{F}{\underset{F}{S}}{=}NR$ |
| | | | Fluorosulfonylamides | Iminofluorosulfonylamides | Bisiminofluorosulfonylamides | | Sulfuroxydifluorideimide | Iminosulfurdifluorideimides |
| | IV |  $F{-}\overset{\odot}{\underset{O}{S}}{-}OH$ |  $F{-}\overset{\odot}{\underset{O}{S}}{-}\overset{H}{N}R$ |  $F{-}\overset{\odot}{\underset{\underset{N-R}{\Vert}}{S}}{-}\overset{H}{N}R$ | |  $\odot SF_2O$ |  $HN{=}\overset{F}{\underset{F}{S}}\odot$ | |
| | | | Fluorosulfinicamides | Iminofluorosulfinicamides | | | Sulfurdifluorideimides | |
| | II |  $F\overset{\odot}{\underset{\odot}{S}}{-}OH$ |  $F{-}\overset{\odot}{\underset{\odot}{S}}{-}\overset{H}{N}R$ | | | — | — | |
| | | | Fluorosulfenicamides | | | | | |

*continued*

TABLE III—*Continued*

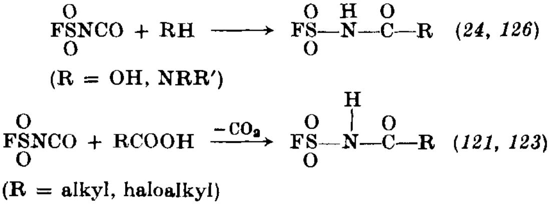
| Acid | Oxidation state | Parent acid | Nitrogen derivatives | Parent oxifluoride | Nitrogen derivatives |
|---|---|---|---|---|---|
| Dibasic | VI |  $F-\overset{O}{\underset{O}{S}}-OH$ |  $F-\overset{O}{\underset{\underset{NH}{\Vert}}{S}}-O-H \longrightarrow F-\overset{O}{\underset{\underset{NH_2}{\vert}}{S}}O$<br>Fluorosulfonicamide<br> $F\overset{O}{\underset{\underset{NH}{\Vert}}{S}}-\overset{H}{N}-R \longrightarrow F\overset{O}{\underset{\underset{NH_2}{\vert}}{S}}=NR$<br>Iminofluorosulfonicamide<br> $F\overset{\overset{NH}{\Vert}}{\underset{\underset{N-R}{\Vert}}{S}}-\overset{H}{N}R \longrightarrow F\overset{\overset{NH_2}{\vert}}{\underset{\underset{NR}{\Vert}}{S}}=NR$<br>Bisiminofluorosulfonicamide | $OSF_2O$ | $HN=SF_2=NH$<br>Bis(imino)-sulfurdifluorideimide |
|  | IV |  $F-\overset{\odot}{\underset{O}{S}}-OH$ |  $F\overset{\odot}{\underset{\underset{NH}{\Vert}}{S}}-OH \longrightarrow F-\overset{\odot}{\underset{\underset{O}{\Vert}}{S}}-NH_2$<br>Fluorosulfinicamide<br> $F\overset{\odot}{\underset{\underset{NH}{\Vert}}{S}}-\overset{H}{N}R \longrightarrow F-\overset{\odot}{\underset{\underset{NH_2}{\vert}}{S}}=NR$<br>Iminofluorosulfinicamide | $\odot SF_2O$ | — |
| Tribasic | VI |  $F\overset{O}{\underset{O}{S}}-OH$ |  $F\overset{\overset{NH}{\Vert}}{\underset{\underset{NH}{\Vert}}{S}}-OH \longrightarrow F\overset{\overset{NH}{\Vert}}{\underset{\underset{NH_2}{\vert}}{S}}=O$<br>Amidosulfuroxyfluoride-imide<br> $F-\overset{\overset{NH}{\Vert}}{\underset{\underset{NH_2}{\vert}}{S}}=NR$<br>Iminoamidosulfurfluoride-imide | $OSF_2O$ | — |

appears to be that imido groups go over to amides in so far as this is possible.

## 1. *Fluorosulfonylamide Ions* $F\overset{O}{\underset{O}{S}}-\underline{\overline{N}}-R^-$

Since fluorosulfonic acid is one of the strongest known acids (*75*), the fluorosulfonylamides, in which the OH group of $FSO_2OH$ is replaced by —NHR, should also show acidic properties. The acid strength in this case depends on the nature of R and, as would be expected, increases roughly in the order alkyl < carboxy < perfluoroalkyl < derivatives with inorganic groups (e.g., $SO_2F$ or $SO_2CF_3$); the latter will be described in a special section.

Starting mostly from $FSO_2NH_2$ and $FSO_2NCO$, it is possible to prepare a large number of compounds of the type $FSO_2NHR$ (*58*). e.g.,

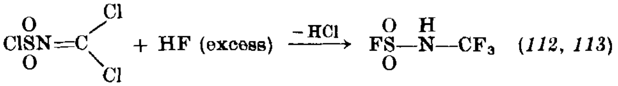


$$F\overset{O}{\underset{O}{S}}NCO + RH \longrightarrow F\overset{O}{\underset{O}{S}}-\overset{H}{N}-\overset{O}{C}-R \quad \text{(24, 126)}$$

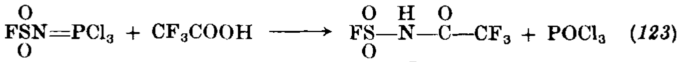
(R = OH, NRR′)

$$F\overset{O}{\underset{O}{S}}NCO + RCOOH \xrightarrow{-CO_2} F\overset{O}{\underset{O}{S}}-\overset{H}{N}-\overset{O}{C}-R \quad \text{(121, 123)} \qquad (17)$$

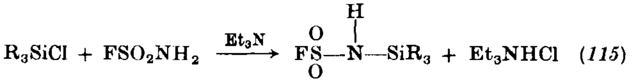
(R = alkyl, haloalkyl)



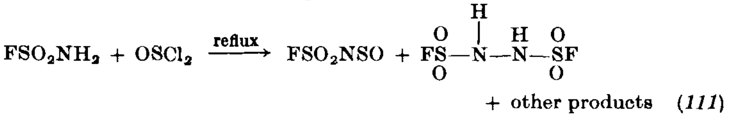
$$Cl\overset{O}{\underset{O}{S}}N=C\begin{matrix}Cl\\Cl\end{matrix} + HF\ \text{(excess)} \xrightarrow{-HCl} F\overset{O}{\underset{O}{S}}-\overset{H}{N}-CF_3 \quad \text{(112, 113)} \qquad (18)$$



$$F\overset{O}{\underset{O}{S}}N=PCl_3 + CF_3COOH \longrightarrow F\overset{O}{\underset{O}{S}}-\overset{H}{N}-\overset{O}{C}-CF_3 + POCl_3 \quad \text{(123)} \qquad (19)$$

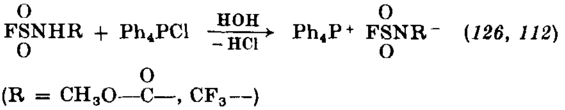


$$R_3SiCl + FSO_2NH_2 \xrightarrow{Et_3N} F\overset{O}{\underset{O}{S}}-\overset{H}{N}-SiR_3 + Et_3NHCl \quad \text{(115)} \qquad (20)$$



$$FSO_2NH_2 + OSCl_2 \xrightarrow{\text{reflux}} FSO_2NSO + F\overset{O}{\underset{O}{S}}-\overset{H}{N}-\overset{H}{N}-\overset{O}{\underset{O}{S}}F + \text{other products} \quad \text{(111)} \qquad (21)$$

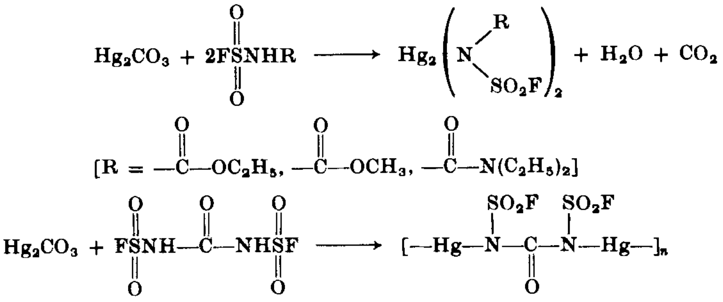
The acidic character of the above compounds may be shown in part by the formation of the corresponding salts with $Ph_4PCl$ or $Ph_4AsCl$ in aqueous solution, e.g.,



$$F\overset{O}{\underset{O}{S}}NHR + Ph_4PCl \xrightarrow[-HCl]{HOH} Ph_4P^+\ F\overset{O}{\underset{O}{S}}NR^- \quad \text{(126, 112)} \qquad (22)$$

$$(R = CH_3O-\overset{O}{C}-,\ CF_3-)$$

Mercury salts are obtained by reaction with $Hg_2CO_3$ in benzene (*15*):



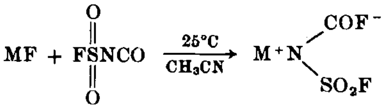
$$Hg_2CO_3 + 2FS(O)_2NHR \longrightarrow Hg_2\left(N\begin{smallmatrix}R\\SO_2F\end{smallmatrix}\right)_2 + H_2O + CO_2$$

$$[R = -C(O)-OC_2H_5,\ -C(O)-OCH_3,\ -C(O)-N(C_2H_5)_2]$$

$$Hg_2CO_3 + FS(O)_2NH-C(O)-NHS(O)_2F \longrightarrow [-Hg-N(SO_2F)-C(O)-N(SO_2F)-Hg-]_n$$

(23)

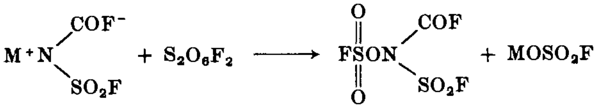
A very simple way for preparing salts of the type $M^+N\begin{smallmatrix}COF^-\\SO_2F\end{smallmatrix}$ is by reaction of $FSO_2NCO$ with alkali fluorides (*110*):



$$MF + FS(O)_2NCO \xrightarrow[CH_3CN]{25°C} M^+N\begin{smallmatrix}COF^-\\SO_2F\end{smallmatrix}$$

(M = Na, K, Cs) (24)

Transfer of the $N\begin{smallmatrix}COF\\SO_2F\end{smallmatrix}$ group takes place in the reaction of the alkali metal salts with $S_2O_6F_2$ (*110*):



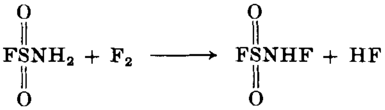
$$M^+N\begin{smallmatrix}COF^-\\SO_2F\end{smallmatrix} + S_2O_6F_2 \longrightarrow FS(O)_2ON\begin{smallmatrix}COF\\SO_2F\end{smallmatrix} + MOSO_2F$$

(25)

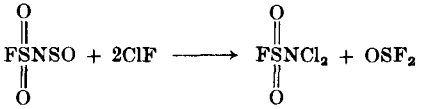
The reaction should occur by a radical mechanism rather than by an ionic.

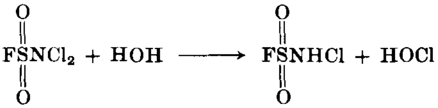
The N-halogen derivatives $FS(O)_2-NHX$ are particularly interesting.

Whereas $FS(O)_2NHF$ results from direct fluorination of $FS(O)_2NH_2$ (*114*),


$$F\underset{O}{\overset{O}{S}}NH_2 + F_2 \longrightarrow F\underset{O}{\overset{O}{S}}NHF + HF \qquad (26)$$

the corresponding N—Cl compound is obtained by hydrolysis of the dichloroamine (*117*),

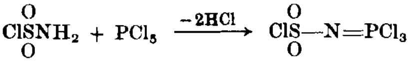

$$F\underset{O}{\overset{O}{S}}NSO + 2ClF \longrightarrow F\underset{O}{\overset{O}{S}}NCl_2 + OSF_2 \qquad (27)$$

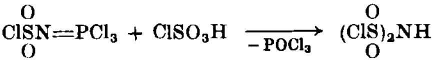

$$F\underset{O}{\overset{O}{S}}NCl_2 + HOH \longrightarrow F\underset{O}{\overset{O}{S}}NHCl + HOCl \qquad (27a)$$

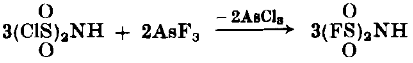
No salts of $F\underset{O}{\overset{O}{S}}NHF$ have been described, but the chlorine derivative has been isolated in the form of its tetraphenylphosphonium or arsonium salts $Ph_4M^+N{<}^{Cl}_{SO_2F}$ (M = P, As).

If a second sulfonyl group ($FSO_2$, $CF_3SO_2$) is introduced as the substituent R in the fluorosulfonylamide $F\underset{O}{\overset{O}{S}}NHR$, there is a drastic increase in the acid strength [p$K_a$ ($FSO_2NHSO_2F$) = 1.28 (*132*)].

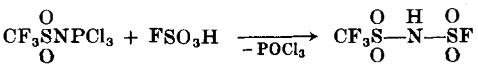
The bis(fluorosulfonyl)amides are best prepared by reaction of $(ClSO_2)_2NH$ with $AsF_3$ (*136*) [other preparative methods are given in (Ref. *58*)]:


$$Cl\underset{O}{\overset{O}{S}}NH_2 + PCl_5 \xrightarrow{-2HCl} Cl\underset{O}{\overset{O}{S}}{-}N{=}PCl_3 \qquad (28a)$$

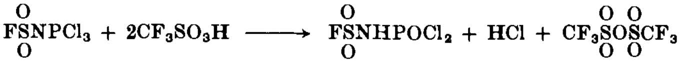

$$Cl\underset{O}{\overset{O}{S}}N{=}PCl_3 + ClSO_3H \xrightarrow[-POCl_3]{} (Cl\underset{O}{\overset{O}{S}})_2NH \qquad (28b)$$


$$3(Cl\underset{O}{\overset{O}{S}})_2NH + 2AsF_3 \xrightarrow{-2AsCl_3} 3(F\underset{O}{\overset{O}{S}})_2NH \qquad (28c)$$

The compound $CF_3SO_2NHSO_2F$ is obtained by the following reaction (*122*):


$$CF_3\underset{O}{\overset{O}{S}}NPCl_3 + FSO_3H \xrightarrow[-POCl_3]{} CF_3\underset{O}{\overset{O}{S}}{-}\overset{H}{N}{-}\underset{O}{\overset{O}{S}}F \qquad (29)$$

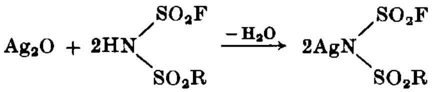
The reverse route using $CF_3SO_3H$ does not, however, give the desired product (*122*):



$$\mathrm{F\overset{O}{\underset{O}{S}}NPCl_3 + 2CF_3SO_3H \longrightarrow F\overset{O}{\underset{O}{S}}NHPOCl_2 + HCl + CF_3\overset{O}{\underset{O}{S}}O\overset{O}{\underset{O}{S}}CF_3} \qquad (29a)$$

Bissulfonylamides react with metallic oxides and carbonates to give the corresponding salts:

$$\mathrm{M_2CO_3 + 2HN(SO_2F)_2 \longrightarrow 2M^+N(SO_2F)_2^- + H_2O + CO_2} \quad (132, 15) \qquad (30)$$
$[\mathrm{M = Na, K, Cs, Hg(I)}]$



$$\mathrm{Ag_2O + 2HN}\begin{array}{l}\diagup SO_2F\\ \diagdown SO_2R\end{array} \xrightarrow{-H_2O} \mathrm{2AgN}\begin{array}{l}\diagup SO_2F\\ \diagdown SO_2R\end{array} \quad (132, 122) \qquad (30a)$$

$(\mathrm{R = F, CF_3})$

They cleave the tin–carbon bond in $Sn(CH_3)_4$ in the same way as do strong oxy acids (*94*):

$$\mathrm{Sn(CH_3)_4 + HN(SO_2F)_2 \longrightarrow (CH_3)_3SnN(SO_2F)_2 + CH_4} \qquad (31)$$

An analogous behavior is also observed in the reaction with xenon difluoride, and this led recently to the synthesis of the first noble gas–nitrogen compound (*84*):

$$\mathrm{XeF_2 + HN(SO_2F)_2 \xrightarrow[0°C/4d.\ -HF]{CF_2Cl_2} \underset{89.2\%}{FXeN(SO_2F)_2}} \qquad (32)$$

Bis(fluorosulfonyl)aminoxenon fluoride is a white solid that decomposes quantitatively at 70° according to (*84*):

$$\mathrm{2FXeN(SO_2F)_2 \longrightarrow Xe + XeF_2 + [(FSO_2)_2N]_2} \qquad (33)$$

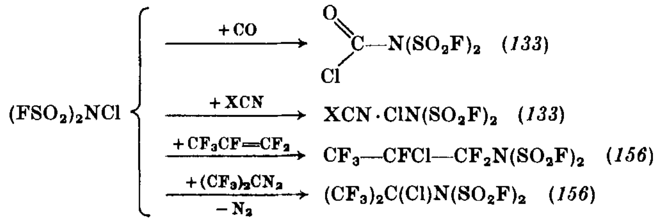
The existence of the xenon compound shows that the $\mathrm{F\overset{O}{\underset{O}{S}}{-}\overline{\underline{N}}{-}\overset{O}{\underset{O}{S}}F^-}$ ion is extraordinarily stable and has a high electronegativity. It resembles the halogens in its behavior, the radicals combining to form a dimer (*133*); with fluorine and chlorine the "interhalogen" compounds $(FSO_2)_2NF$ (*136*) and $(FSO_2)_2NCl$ are obtained (*133*):

$$\mathrm{2(FSO_2)_2NCl \xrightarrow{UV} [(FSO_2)_2N]_2 + Cl_2} \qquad (34)$$

$$\mathrm{(FSO_2)_2NH + F_2 \longrightarrow (FSO_2)_2NF + HF} \qquad (35)$$

$$\mathrm{(FSO_2)_2N^-Ag^+ + Cl_2 \longrightarrow (FSO_2)_2NCl + AgCl} \qquad (36)$$

The N—Cl compound prepared from the $(FSO_2)_2\overline{\underline{N}}^-$ ion provides a key to the synthesis of organobis(fluorosulfonyl)amides. It may be added by either a radical or a polar mechanism to multiple bonds. Insertion of methylenes into the N—Cl bond is likewise possible.



$$(FSO_2)_2NCl \left\{ \begin{array}{ll} \xrightarrow{+CO} \overset{O}{\underset{Cl}{C}}\!-\!N(SO_2F)_2 & (133) \\ \xrightarrow{+XCN} XCN\cdot ClN(SO_2F)_2 & (133) \\ \xrightarrow{+CF_3CF{=}CF_2} CF_3{-}CFCl{-}CF_2N(SO_2F)_2 & (156) \\ \xrightarrow[-N_2]{+(CF_3)_2CN_2} (CF_3)_2C(Cl)N(SO_2F)_2 & (156) \end{array} \right. \qquad (37)$$

Alkyl halides will also react directly with the silver salt (*132*):

$$AgN(SO_2F)_2 + CH_3I \longrightarrow CH_3N(SO_2F)_2 + AgI \qquad (38)$$

In this way it was possible to introduce the $N(SO_2F)_2$ group into transition metal chemistry (*46*, *96*):

$$M(CO)_5Br + AgN(SO_2F)_2 \xrightarrow[-AgBr]{CH_2Cl_2} M(CO)_5N(SO_2F)_2 \qquad (39)$$
$$(M = Mn, Re)$$

$$Mn(CO)_4\,(Ph_3P, As)Br + AgN(SO_2F)_2 \xrightarrow{-AgBr} Mn(CO)_4\,(Ph_3P, As)N(SO_2F)_2 \qquad (39a)$$

$$C_5H_5Fe(CO)_2I + AgN(SO_2F)_2 \xrightarrow{-AgI} C_5H_5Fe(CO)_2N(SO_2F)_2 \qquad (39b)$$

$$C_5H_5Cr(NO)_2Cl + AgN(SO_2F)_2 \xrightarrow{-AgCl} C_5H_5Cr(NO)_2N(SO_2F)_2 \qquad (39c)$$

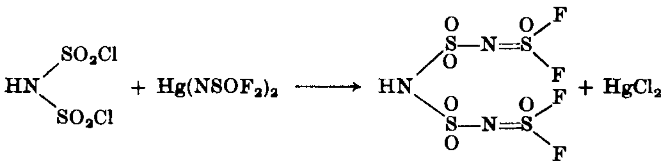
The transition metal–nitrogen bond in these complexes is highly polar, and, in their reactions with ligands such as $CH_3CN$, $Ph_3P$, and $Ph_3As$, the first step is always exchange of the bis(fluorosulfonyl)amino group with formation of ionic compounds (*46*, *96*):

$$M(CO)_5N(SO_2F)_2 + CH_3CN \longrightarrow [M(CO)_5CH_3CN]^+N(SO_2F)_2^- \qquad (40)$$

$$M(CO)_5N(SO_2F)_2 + Ph_3P \longrightarrow [M(CO)_5(Ph_3P)]^+N(SO_2F)_2^- \qquad (40a)$$
$$(M = Mn, Re)$$

$$C_5H_5Fe(CO)_2N(SO_2F)_2 + L \longrightarrow [C_5H_5Fe(CO)_2L]^+N(SO_2F)_2^- \qquad (40b)$$
$$(L = CH_3CN, Ph_3P)$$

Closely related to the acids discussed above is compound *SS*-bis-(sulfur oxydifluorideimidosulfonyl)amide (*17*):



(41)

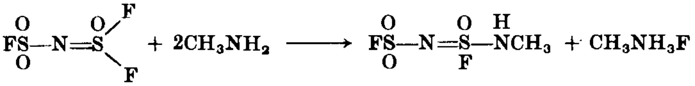
In its reactions it behaves like the other bis(sulfonyl) amides (*17*):

$$HN(SO_2NSOF_2)_2 \left\{ \begin{array}{l} \xrightarrow{+AgCF_3COO} Ag^+N(SO_2NSOF_2)_2^- \\ \xrightarrow{+Li-n\text{-}C_4H_9} Li^+\ N(SO_2NSOF_2)_2^- \\ \xrightarrow[\text{in } H_2O]{+Ph_4MCl} Ph_4M^+\ N(SO_2NSOF_2)_2^- \end{array}\right. \qquad (42)$$

(M = P, As)

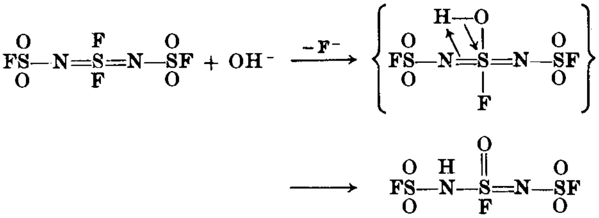
*a. Iminofluorosulfonylamide Ions,* $F\underset{\underset{NR}{\|}}{\overset{O}{S}}-\overline{\underline{N}}-R'^-$. In the iminofluorosulfonylamides, an oxygen atom of the fluorosulfonylamide is formally replaced by an isosteric RN= group. They may be prepared by the following methods:

i. Decomposition of sulfur oxydifluoride imides with primary amines (*119*),



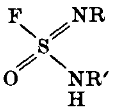
$$FSO_2-N=S(O)F_2 + 2CH_3NH_2 \longrightarrow FSO_2-N=\overset{O}{\underset{F}{S}}-\overset{H}{N}CH_3 + CH_3NH_3F \qquad (43)$$

ii. By hydrolysis of bis(imino)sulfur difluorides (*127*),



$$FSO_2-N=SF_2=N-SO_2F + OH^- \xrightarrow{-F^-} \left\{ FSO_2-N=\overset{H-O}{\underset{F}{S}}=N-SO_2F \right\} \longrightarrow FSO_2-\overset{H}{N}-\overset{\overset{O}{\|}}{\underset{F}{S}}=N-SO_2F \qquad (44)$$

The hydrolysis product is isolated as the tetraphenylphosphonium salt. Replacement of one oxygen in the fluorosulfonylamides by imino groups reduces the acidity, but it is possible by changing R and R′ in



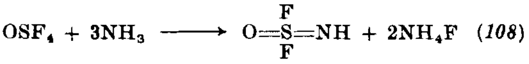
to vary the acid strength at will.

*b. Bis(imino)fluorosulfonylamide Ions,* $F-\underset{\underset{NR'}{\|}}{\overset{\overset{NR}{\|}}{S}}-\overline{\underline{N}}-R''^-$. Although the reactions of sulfur difluoride diimides with secondary amines have been described (*118*),

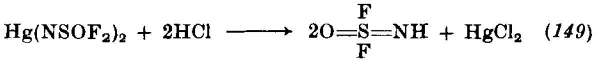
$$RN{=}\overset{F}{\underset{F}{S}}{=}NR + 2R'_2NH \longrightarrow RN{=}\overset{F}{\underset{NR'_2}{S}}{=}NR + R'_2NH_2F \qquad (45)$$

there are no reports on the reactions with primary amines, which would give the desired type of compound.

*c. Sulfur Oxydifluorideimide Ion*, $O{=}\overset{F}{\underset{F}{S}}{=}\overline{\underline{N}}^-$. Several methods are available for preparing the free acid:

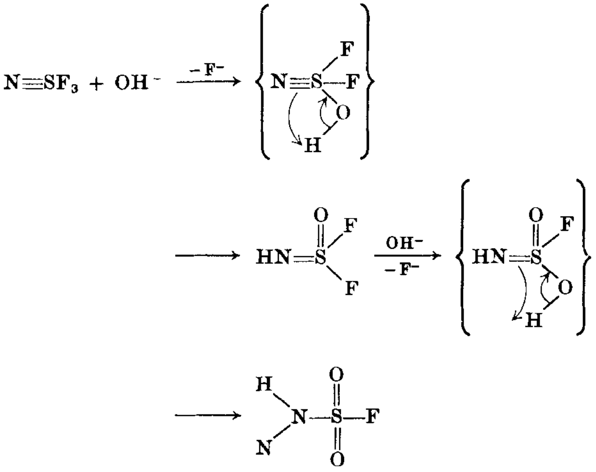


$$OSF_4 + 3NH_3 \longrightarrow O{=}\overset{F}{\underset{F}{S}}{=}NH + 2NH_4F \quad (108) \qquad (46)$$



$$Hg(NSOF_2)_2 + 2HCl \longrightarrow 2O{=}\overset{F}{\underset{F}{S}}{=}NH + HgCl_2 \quad (149) \qquad (46a)$$

Sulfur oxydifluoride imide has also been detected as a product of the hydrolysis of $NSF_3$ (*124*). This reaction is especially interesting as it illustrates a general principle in sulfur–nitrogen chemistry. It has been found in all hydrolysis reactions so far investigated that proton migration occurs if a sulfur–oxygen double bond can form at the expense of a sulfur–nitrogen multiple bond:



(47)

This reaction principle is not restricted to linear thiazenes but is also encountered in S—N heterocycles (Section V, A, 2).

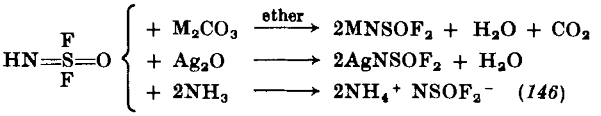
Salts of sulfur oxydifluoride imide are obtained by cleavage of the

CN bond in $COFNSOF_2$ or of the SiN bond in $R_3SiNSOF_2$ (*59*, *64*, *134*, *148*):

$$COFNSOF_2 + CsF(HgF_2) \xrightarrow{-COF_2} Cs^+\ NSOF_2^-\ [Hg(NSOF_2)_2] \tag{48}$$

$$2R_3SiNSOF_2 + HgF_2 \xrightarrow{-2R_3SiF} Hg(NSOF_2)_2 \tag{48a}$$

The method that makes use of the acid character of the imide is, however, particularly simple (*43*):



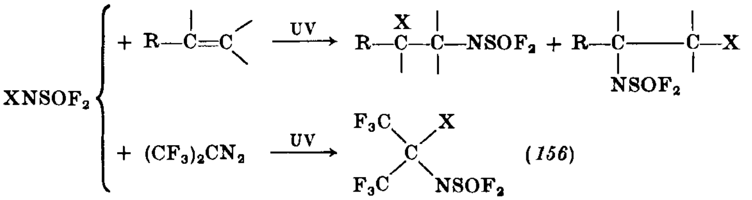
$$HN{=}\overset{F}{\underset{F}{S}}{=}O \begin{cases} + M_2CO_3 \xrightarrow{\text{ether}} 2MNSOF_2 + H_2O + CO_2 \\ + Ag_2O \longrightarrow 2AgNSOF_2 + H_2O \\ + 2NH_3 \longrightarrow 2NH_4^+\ NSOF_2^-\ \ (146) \end{cases} \tag{49}$$

Decomposition of the cesium, mercury, or silver salts with halogens leads to the corresponding N–halogen compounds (*43*, *59*, *134*, *149*):

$$M(NSOF_2)_n + nX_2 \longrightarrow nXNSOF_2 + MX_n \tag{50}$$

$(n = 1,2;\ M = Cs, Ag, Hg;\ X = F, Cl, Br, I)$

These N–halogen compounds provide a route to organosulfur oxydifluoride imides:



(*78*, *95*, *156*) (51)

(*156*)

(X = Cl)

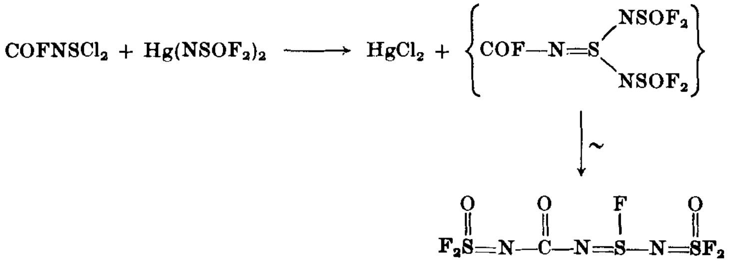
The mercury salt is very suitable for the preparation of inorganic sulfur oxydifluoride imides, and the $NSOF_2$ ion can be transferred to a large number of elements by reaction with the corresponding halides (*18*, *72*, *76*, *129*, *153*):

$$MCl_n + (n/2)Hg(NSOF_2)_2 \xrightarrow[CH_2Cl_2]{40^\circ} M(NSOF_2)_n + (n/2)HgCl_2 \tag{52}$$

$M$ = B Sb Sb OSe $OCNSO_2^-$ $CH_3O{-}S(O){-}$ $Cl_3PN{-}SO_2{-}$
$n$ = 3 3 "5" 2 1 1 1

$M$ = P As $(CH_3)_{4-n}Si$ OS $FSO_2NS$ $(CH_3)_3Sn$
$n$ = 3 3 1–4 2 2 1

An interesting rearrangement is observed in the reaction with $COFNSCl_2$ (*18*):



(53)

In many cases $AgNSOF_2$ has proved to be a better reagent, because AgCl is less volatile and more insoluble than $HgCl_2$ and, thus, no separation problems arise. Alkyltin, phosphoryl, and thiophosphoryl derivatives have been prepared in this way, the composition of the products depending on the stoichiometric ratio taken (*44*):

$$AgNSOF_2 \begin{cases} + (CH_3)_2SnX_2 \longrightarrow R_2Sn(NSOF_2)_2,\ R_2SnClNSOF_2,\ R_2SnBrNSOF_2 \\ + OPCl_3 \longrightarrow OP(NSOF_2)_3, OPCl(NSOF_2)_2, OPCl_2(NSOF_2) \\ + OPFCl_2 \longrightarrow OPF(NSOF_2)_2, OPFCl(NSOF_2)_2 \\ + SPCl_3 \longrightarrow SP(NSOF_2)_3, SPCl(NSOF_2)_2, SPF(NSOF_2)_2, SPCl_2NSOF_2 \end{cases} \qquad (54)$$

The silver salt has also been used to introduce the $NSOF_2$ group into transition metal chemistry (*97*):

$$\begin{tikzcd} Re(CO)_5Br + AgNSOF_2 \arrow[r, "RT", "CH_2Cl_2"'] & Re(CO)_5NSOF_2 + AgBr \arrow[d, "90°C,\ n\text{-heptane}"] \\ & \tfrac{1}{2}[Re(CO)_4NSOF_2]_2 + 2CO \end{tikzcd} \qquad (55)$$

$$2Mn(CO)_5Br + 2AgNSOF_2 \xrightarrow[CH_2Cl_2]{RT} [Mn(CO)_4NSOF_2]_2 + 2AgBr + 2CO \qquad (55a)$$

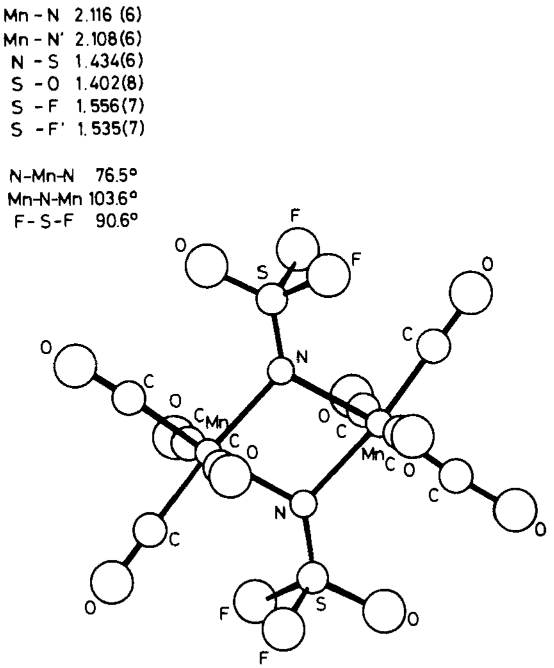
Compounds $C_5H_5Fe(CO)_2NSOF_2$ and $C_5H_5Cr(NO)_2NSOF_2$ may be similarly prepared from the corresponding iodide or chloride (*45*).

Structural investigations show that bridging in the dimeric Re and Mn compounds occurs only through the nitrogen atom of the $NSOF_2$ group (*20*). Bond distances and angles in the geminal $NSOF_2$ group of $Re(CO)_5NSOF_2$ hardly deviate from the values found for the bridging ligand itself (Figs. 1 and 2).

Dimers also occur with substituted Mn tetracarbonyl halogenides (*45*):

$$2Mn(CO)_4(Ph_3X)Br + 2AgNSOF_2 \longrightarrow [Mn(CO)_3(Ph_3X)NSOF_2]_2 + 2AgBr + 2CO$$

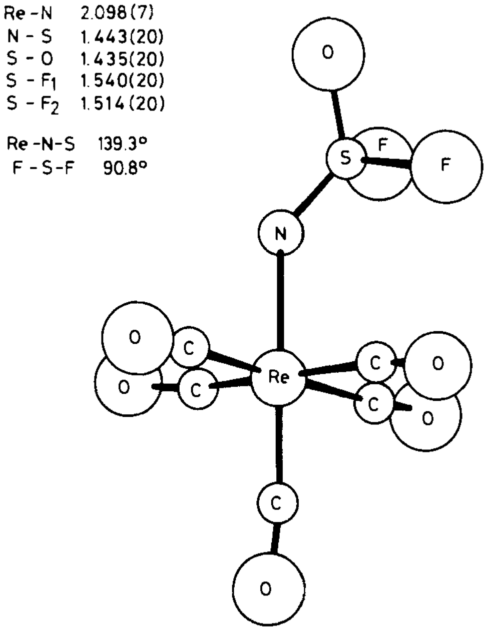
$$(X = P, As, Sb) \qquad (56)$$



| | |
|---|---|
| Mn - N | 2.116 (6) |
| Mn - N' | 2.108(6) |
| N - S | 1.434(6) |
| S - O | 1.402(8) |
| S - F | 1.556(7) |
| S - F' | 1.535(7) |

| | |
|---|---|
| N-Mn-N | 76.5° |
| Mn-N-Mn | 103.6° |
| F-S-F | 90.6° |

FIG. 1. Molecular structure of $[Mn(CO)_4NSOF_2]_2$.

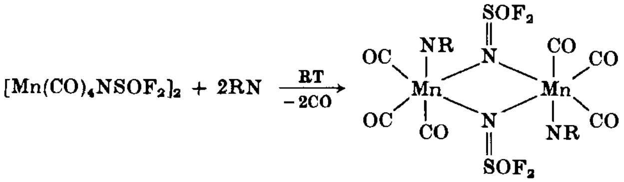


| | |
|---|---|
| Re - N | 2.098(7) |
| N - S | 1.443(20) |
| S - O | 1.435(20) |
| S - $F_1$ | 1.540(20) |
| S - $F_2$ | 1.514(20) |

| | |
|---|---|
| Re-N-S | 139.3° |
| F - S - F | 90.8° |

FIG. 2. Molecular structure of $Re(CO)_5NSOF_2$.

The bridge structure remains unchanged in the reaction of $[Mn(CO)_4NSOF_2]_2$ with nitrogen bases (*94*):



(57)

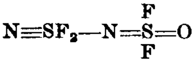
(NR = pyr, $CH_3CN$)

The rhenium compound does not react under these conditions. With $Ph_3P$ and $Ph_3As$, bridge cleavage occurs (*94*):

$$[M(CO)_4NSOF_2]_2 + 4Ph_3X \longrightarrow M(CO)_3(Ph_3X)_2NSOF_2 + 2CO \qquad (58)$$

(M = Mn, Re; X = P, As)

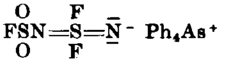
*d. Iminosulfur Difluorideimide Ions*, $RN{=}\overset{F}{\underset{F}{S}}{=}N^-$. One representative of this class of compound is prepared by the hydrolysis of



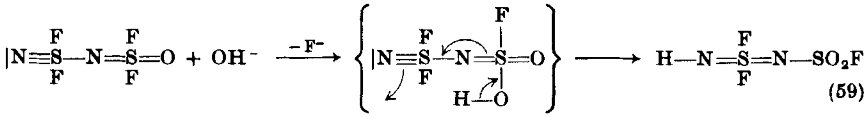
$$N{\equiv}SF_2{-}N{=}\overset{F}{\underset{F}{S}}{=}O$$

(*54*)

the acid being isolated as the tetraphenylarsonium salt,

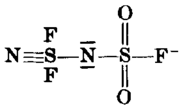


$$FS\overset{O}{\underset{O}{}}N{=}\overset{F}{\underset{F}{S}}{=}\overline{\underline{N}}^- \; Ph_4As^+$$



(59)

Structural investigations (Fig. 3) show clearly that there are three different S—N distances, the bond to the geminal nitrogen being the shortest (1.439 Å), followed by that between the bridge nitrogen atom and the $FSO_2$ group (1.517 Å). These S–N bond distances suggest that the structure of this special iminosulfur difluoride is better described as difluorothiazyl fluorosulfonylamide



$$N{\equiv}\overset{F}{\underset{F}{S}}{-}\overline{\underline{N}}^-{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}F^-$$

(the $N{\equiv}SF_2^-$ group being isoelectronic to $FSO_2^-$) This ion should be structurally closely related to $(FSO_2)_2N^-$.

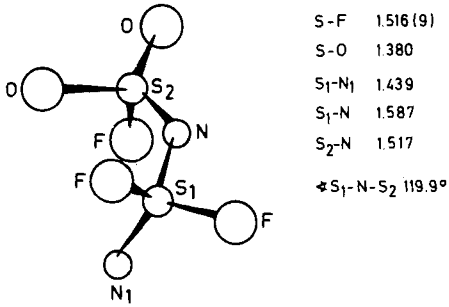
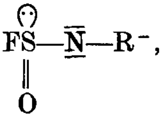
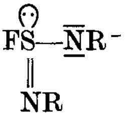
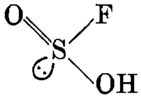
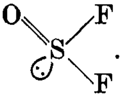
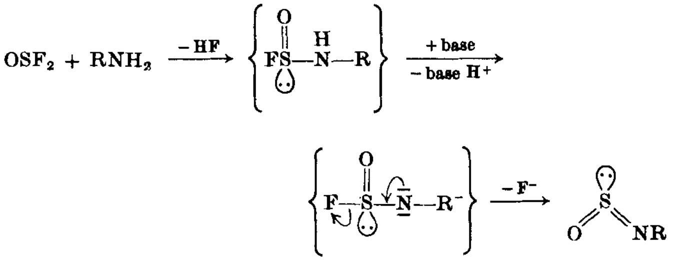


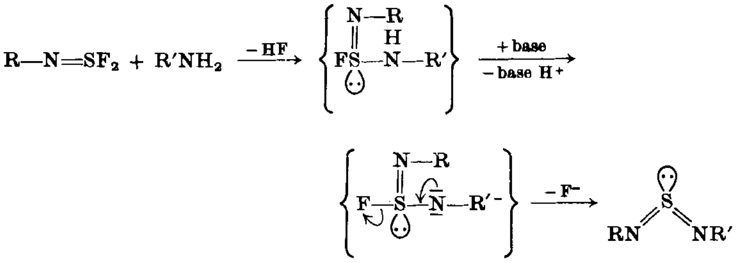
FIG. 3. Molecular structure of $NSF_2NSO_2F^-$ (*19*).

## 2. *Fluorosulfinamide*,  $FS(=O)-\overline{N}-R^-$, *and Iminofluorosulfinamide Ions*,  $FS(=NR)-\overline{N}R^-$

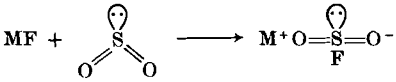
If the systematic treatment is continued for S(IV) in the same way as for S(VI), the corresponding starting point is fluorosulfinic acid  or thionyl fluoride . In this case the theoretical possibilities for the formation of tetrahedrally coordinated anions are limited since the free pair of electrons can occupy the position of the double-bonded oxygen and also that of the imino group. As numerous examples show, sulfur(IV) has some tendency to assume a coordination number of 3. Fluorosulfinic acid itself decomposes to HF and OSO (*145*), and similar reactions are to be expected for the sulfur(IV)–nitrogen system:



(*69*) (60)


(32) (61)

On the other hand, salts of fluorosulfinic acid may be prepared by addition of $F^-$ to $SO_2$ (*144, 145*):


(62)

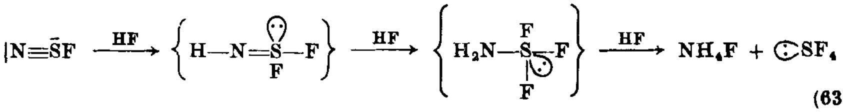
If one or both of the oxygen atoms in $SO_2$ are replaced by the isosteric RN= group, the $F^-$ acceptor property of the central sulfur atom is reduced. Reaction analogous to that in Eq. (62) might be successful only if R = perfluoroalkyl or an inorganic group.

a. *Sulfur Difluorideimide Ion*, $:\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{S}}}{=}\bar{\underline{\mathrm{N}}}^{-}$. The free acid $\mathrm{HN}{=}\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{S}}}:$ is unstable. Earlier unsuccessful attempts to prepare it have recently been confirmed:

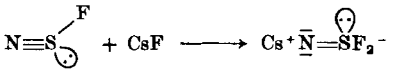
$$\mathrm{NH_3 + SF_4 \xrightarrow{-NH_4F} \{HN{=}SF_2\} \xrightarrow[-NH_4F]{NH_3} N{\equiv}\bar{S}{-}F} \quad (58) \qquad (63)$$

$$\mathrm{Ph_3P{=}NH + SF_4 \xrightarrow{-Ph_3PF_2} \{HN{=}SF_2\} \xrightarrow{-HF} N{\equiv}\bar{S}{-}F} \quad (2) \qquad (63a)$$

the NSF is decomposed in liquid HF (*94*):


(63b)

Salts of sulfur difluorideimide may, however, be prepared (i) by addition of $F^-$ to NSF (*50, 134*),


(64)

or (ii) by cleavage of the C—N bond in acylsulfur difluorideimides with CsF or $HgF_2$ (*52, 60, 134*),

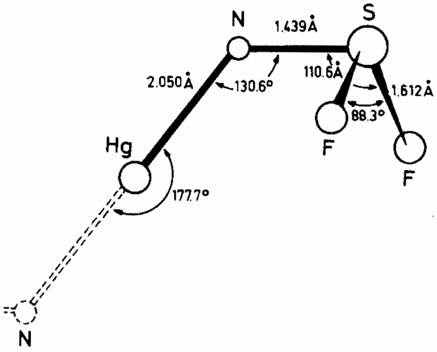
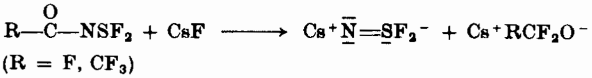
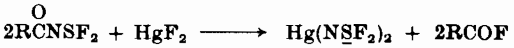


FIG. 4. Molecular structure of $Hg(NSF_2)_2$.



$$\underset{(R\,=\,F,\,CF_3)}{R{-}\overset{O}{C}{-}NSF_2} + CsF \longrightarrow Cs^+\overline{\underline{N}}{=}\underline{S}F_2^- + Cs^+RCF_2O^- \qquad (64a)$$



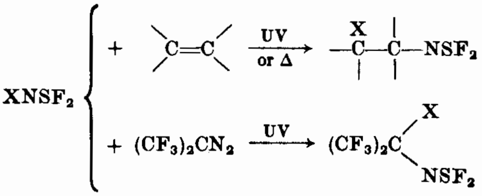
$$2R\overset{O}{C}NSF_2 + HgF_2 \longrightarrow Hg(N\underline{S}F_2)_2 + 2RCOF \qquad (64b)$$

The structure of the mercury salt has been determined (*80*) (Fig. 4). Reaction of the mercury salt with chlorides has so far resulted in chlorine–fluorine exchange and the splitting off of NSF, but not in transfer of the $NSF_2$ group. With halogens, the corresponding N-halogen compounds are obtained:

$$\underset{(X\,=\,Cl,\,Br)}{CsNSF_2 + X_2} \longrightarrow CsX + XNSF_2 \quad (\mathit{134}) \qquad (65)$$

$$\underset{(X\,=\,F,\,Cl,\,Br,\,I)}{Hg(NSF_2)_2 + 2X_2} \longrightarrow HgX_2 + 2XNSF_2 \quad (\mathit{60,\ 61}) \qquad (65a)$$

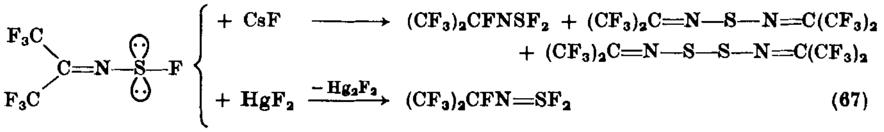
These compounds open up a valuable route to organosulfur difluoride-imides, as has been demonstrated with $ClNSF_2$ and $BrNSF_2$ (*58*, *156*):



(66)

### 3. *Fluorosulfenamide Ions*, $FS{-}\overline{\underline{N}}{-}R^-$

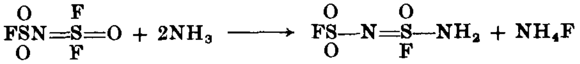
The only possible type of a tetrahedrally coordinated S(II) anion, $F{-}S{-}\overline{\underline{N}}R^-$, has not so far been synthesized and, from the known instability of sulfur(II)–fluorine compounds such a preparation appears to be very unlikely. Attempts to add fluorine ions to the C=N bond in $(CF_3)_2C{=}N{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}F$ (*158*) resulted in slow decomposition of the sulfenyl fluoride (*157*):



(67)

*4. Anions of Di- and Tribasic Acids*

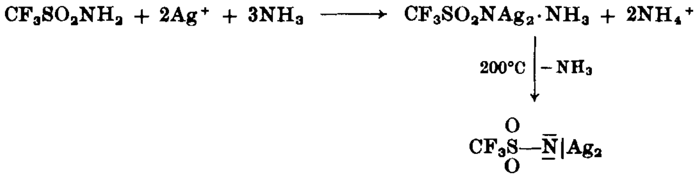
As Table III shows, all of the theoretically possible dibasic acids [except $F_2S(NH)_2$] occur as amines. In addition to $F\overset{O}{\underset{O}{S}}NH_2$, only $F\overset{O}{\underset{O}{S}}{-}N{=}\overset{O}{\underset{F}{S}}{-}NH_2$ has so far been prepared (*127*):



$$F\overset{O}{\underset{O}{S}}N{=}\overset{F}{\underset{F}{S}}{=}O + 2NH_3 \longrightarrow F\overset{O}{\underset{O}{S}}{-}N{=}\overset{O}{\underset{F}{S}}{-}NH_2 + NH_4F \tag{68}$$

The reaction of sulfur difluoridediimides with ammonia to give the corresponding bisimino derivatives, $R{-}N{=}\overset{\overset{\displaystyle N{-}R}{\|}}{\underset{\underset{\displaystyle F}{|}}{S}}{-}NH_2$, has not been described, nor is *SS*-difluorosulfur diimide or its salts known. Work on $F\overset{\cdot\cdot}{\underset{O}{S}}NH_2$ (*69*) should be checked as this compound would be expected to decompose very rapidly to HNSO and HF. Interaction of $HN{=}SOF_2$ with $NH_3$ gives the ammonium salt $NH_4{}^+NSOF_2{}^-$ (*146*) rather than the amino derivative.

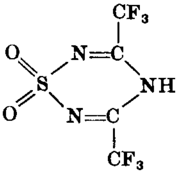
Aminosulfonyl compounds exhibit acidic properties, as is shown, for example, in the case of $CF_3SO_2NH_2$ (*14*):



$$\begin{array}{c} CF_3SO_2NH_2 + 2Ag^+ + 3NH_3 \longrightarrow CF_3SO_2NAg_2\cdot NH_3 + 2NH_4{}^+ \\ {\scriptstyle 200^\circ C}\Big\downarrow{\scriptstyle -NH_3} \\ CF_3\overset{O}{\underset{O}{S}}{-}\overline{\underline{N}}|Ag_2 \end{array} \tag{69}$$

Compound $FSO_2NH_2$, on the other hand, is decomposed by alkali. The desired silver salt cannot be isolated by reaction with $CF_3COOAg$.

At 140° to 160°C, the sulfur-containing heterocycle



is obtained in 10–15% yield (in addition to $CF_3COF$, $CF_3CN$ and $CO_2$) (*46*). This compound is formed in better yield from $ClSO_2NPCl_3$ and $CF_3COOH$ (*116*).

## IV. Acyclic Nitrogen–Sulfur–Fluorine Cations

The coordination number 4 dominates the chemistry of nitrogen–sulfur–fluorine cations. Neutral pentacoordinated compounds always split off fluorine ions on treatment with Lewis acids to give tetracoordinated cations. By contrast, it is not possible to prepare threefold coordinated cations from tetracoordinated neutral S(VI) compounds with the aid of Lewis acids. In the case of S(IV), threefold coordinated cations may be obtained by selecting suitable ligands and, in $N{\equiv}S{:}^+$, we even find formal twofold coordination.

### A. TETRACOORDINATED CATIONS

Since the time that ${:}SF_3{}^+$ (*9*, *10*, *142*, *143*) and $O{=}SF_3{}^+$ cations (*142*, *143*) were first prepared by splitting off $F^-$ from the neutral pentacoordinated compounds,

$$OSF_4 + MF_5(BF_3) \longrightarrow OSF_3{}^+\ MF_6{}^-\ (BF_4)^- \tag{70}$$

$${:}SF_4 + MF_5(BF_3) \longrightarrow {:}SF_3{}^+\ MF_6{}^-\ (BF_4)^- \tag{70a}$$

$(M = Sb, As)$

a series of investigations on them have been carried out. Infrared, Raman (*3*, *16*, *42*, *143*) and NMR spectra (*3*, *8*) established that these compounds were indeed salts of the type shown, but only recently have the structures been determined by X-ray analysis (Fig. 5).

It was possible to prepare the first mixed halogen derivative (Fig. 6) by oxidative addition of a chlorine cation to $OSF_2$ (*82*, *83*):

$$O{=}\overset{F}{\underset{F}{S}}{:} + Cl_2F^+AsF_6{}^- \longrightarrow OSF_2Cl^+AsF_6{}^- + ClF \tag{71}$$

Analogous compounds are unknown in S(IV) chemistry. In addition to ${:}SF_3{}^+$ only ${:}SCl_3{}^+$ has been described (*79*):

$$SCl_2 + 2AsF_3 + 2Cl_2 \longrightarrow {:}SCl_3{}^+AsF_6{}^- + AsCl_3 \tag{72}$$

FIG. 5. Structure of Ͼ$SF_3^+$ (*47*) and $OSF_3^+$ cations (*81*).

Addition of NOCl at low temperatures to a solution of $\bar{S}F_3{}^+AsF_6{}^-$ in $SO_2$, followed by excess of $AsF_5$ after completion of the reaction, gives a mixture of $NO^+AsF_6{}^-$, $\bar{S}F_3{}^+AsF_6{}^-$, and $\bar{S}Cl_3{}^+AsF_6{}^-$ (*94*):

$$\begin{tikzcd}
\text{Ͼ}SF_3{}^+AsF_6{}^- + NOCl \arrow[r, "-60^\circ C", "SO_2\ liq."'] & NO^+AsF_6{}^- + \{\text{Ͼ}SF_3Cl\} \arrow[d, "AsF_5"] \\
\text{Ͼ}SF_3{}^+AsF_6{}^- + \text{Ͼ}SCl_3{}^+AsF_6{}^- & \{\text{Ͼ}\overset{+}{S}F_2Cl\ AsF_6{}^-\} \arrow[l]
\end{tikzcd} \qquad (73)$$

Whether the exchange occurs at the stage where the neutral pentacoordinated compound is present or whether the tetracoordinated cation disproportionates is not yet known.

Although replacement of fluorine in the cations by other halogens was possible in only one exceptional case, the existence of a series of known perhaloalkyl (*130*, *137–139*), aryl (*150*), amino (*37*, *53*, *159*, *160*), and aryloxy (*33*, *161*, *131*) derivatives of $OSF_4$ or Ͼ$SF_4$ shows that derivatives of the $OSF_3{}^+$ and Ͼ$SF_3$ cations can certainly be made. In the case of S(VI) it is also possible to replace the doubly bonded oxygen by an RN= group and, thus, obtain iminosulfur trifluoride cations, $RN{=}\overset{+}{S}F_3$.

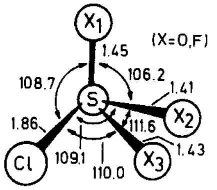


FIG. 6. Structure of the $OSF_2Cl^+$ cation.

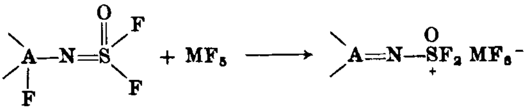
### 1. *Derivatives of the* $OSF_3^+$ *Cation*

Derivatives of the $OSF_3^+$ cation may be prepared in three ways.

a. By cleavage of fluoride ions (i) from pentacoordinated neutral compounds [as in Eq. (70)],

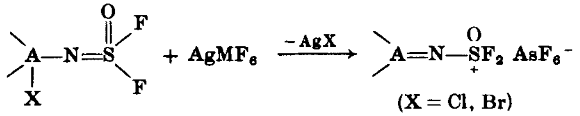
$$R{-}\overset{O}{S}F_3 + MF_5 \longrightarrow R\underset{+}{\overset{O}{S}}F_2\,MF_6^- \qquad (74)$$

(ii) from a neighboring group to an already four-coordinated sulfur,



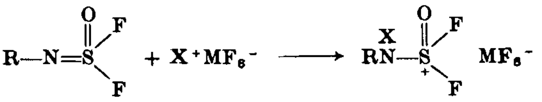
(75)

or



(75a)

b. By addition of cations to tetracoordinated neutral compounds:



(76)

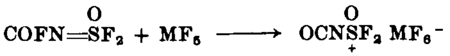
The type of reaction shown in Eq. (74) is possible for all derivatives of $OSF_4$. It would be expected that replacement of one or several fluorine atoms by other groups would increase the ability to donate fluorine ions because of the greater +I effect. This is particularly marked for amino derivatives (*94*):

$$(CH_3)_2NSOF_3 + MF_5 \longrightarrow (CH_3)_2NSOF_2{}^+MF_6^- \qquad (77)$$

(M = As, white solid, m.p. 223°C, or Sb white solid, m.p. 229°C)

These unexpectedly high-melting salts are thermally extraordinarily stable and the vibrational and NMR spectra show discrete anions and cations to be present both in the solid state and in solution.

Fluorformylsulfur oxydifluorideimide reacts according to Eq. (75), losing a fluoride ion of the fluorformyl group (*94*):

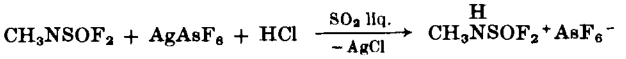


$$COFN{=}\overset{O}{S}F_2 + MF_6 \longrightarrow OCN\underset{+}{\overset{O}{S}}F_2\,MF_6^- \qquad (78)$$

(M = As, Sb)

No stable salt is obtained with $BF_3$. Properties and reactions of the isocyanatosulfur oxydifluoride cation are discussed in connection with the corresponding derivatives of $SF_4$.

The protonation of $CH_3NSOF_2$ is an example of reaction type b [Eq. (76)]:



$$CH_3NSOF_2 + AgAsF_6 + HCl \xrightarrow[-AgCl]{SO_2\ liq.} CH_3\overset{H}{N}SOF_2{}^+AsF_6{}^- \qquad (79)$$

The interaction of cationic transition metal–$SO_2$ complexes (*93*) with this compound (*46*) may possibly be a further example:

$$M(CO)_5Br + AgAsF_6 + CH_3NSOF_2 \xrightarrow[-AgBr]{SO_2\ liq.}$$

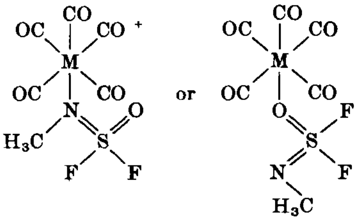
$$[M(CO)_5SO_2]^+AsF_6{}^- + CH_3NSOF_2 \xrightarrow{-SO_2} [M(CO)_5CH_3NSOF_2]^+AsF_6{}^- \qquad (79a)$$

$(M = Mn, Re)$

$$C_5H_5Fe(CO)_2I + AgAsF_6 + CH_3NSOF_2 \xrightarrow[-AgI]{SO_2\ liq.}$$

$$[C_5H_5Fe(CO)_2CH_3NSOF_2]^+AsF_6{}^- \qquad (79b)$$

So far it has been impossible to determine from spectroscopic data if $CH_3NSOF_2$ in these cations is coordinated to the transition metal through nitrogen or oxygen:



Coordination through nitrogen is more probable from what is so far known of the chemistry of such substances.

### 2. *Iminosulfur Trifluoride Cations*, $RN{=}SF_3{}^+$

These cations may be prepared in three different ways. (a) cleavage of fluoride ions from the pentacoordinated sulfur tetrafluorideimides [as in Eq. (70a)],

$$R{-}N{=}SF_4 + MF_5 \longrightarrow RN{=}SF_3{}^+MF_6{}^- \qquad (80)$$

(b) fluorination of sulfur difluoride imides in presence of Lewis acids,

$$R{-}N{=}SF_2 + F_2 + MF_5 \longrightarrow RN{=}SF_3{}^+MF_6{}^- \qquad (81)$$

and (c) addition of cations to the nitrogen of $NSF_3$,

$$NSF_3 + X^+\,MF_6{}^- \longrightarrow X{-}N{=}SF_3{}^+\,MF_6{}^- \qquad (82)$$

Reactions of the types shown in Eqs. (80) and (81) have not yet been fully investigated. On irradiation of sulfur difluoride imides with $OF_2$, sulfur oxydifluorideimides and sulfur difluoride diimides are obtained (*151*):

$$3R{-}NSF_2 + OF_2 \xrightarrow{UV} RNSOF_2 + RNSF_2NR + SF_4 \tag{83}$$

Formation of sulfur tetrafluorideimides is sometimes observed in these reactions. $(CF_3)_2CFNSF_4$ reacts with $AsF_5$ according to Eq. (80):

$$(CF_3)_2CFNSF_4 + AsF_5 \longrightarrow (CF_3)_2CF{-}N{=}\overset{+}{S}F_3AsF_6^- \quad (\mathit{154}) \tag{84}$$

Equation (81) brings together both of the last reactions (oxidation and cation formation).

In the reaction of thiazyl trifluoride, attack by electrophiles on nitrogen plays a major role in addition to the exchange of fluorine atoms on sulfur by nucleophiles. Recent investigations have shown that nitrogen carries a substantial negative charge (*31*, *77*), and this has been used in preparative work involving reactions with Lewis acids (*58*, *56*):

$$NSF_3 \begin{cases} + BF_3 \longrightarrow F_3B{-}NSF_3 & \\ + MF_5 \longrightarrow F_5M{-}NSF_3 & (M = As, Sb) \end{cases} \tag{85}$$

Derivatives of $NSF_3$ behave similarly: No cations are formed, and, as would be expected, sulfur(VI) retains tetracoordination.

Coordinatively unsaturated transition metal complexes react as Lewis acids and add electrophillically (*89*, *98*):

$$\begin{tikzcd} M(CO)_5Br + Ag^+AsF_6^- \arrow[r, "NSF_3\ liq."', "-AgBr"'] & \{M(CO)_5{}^+AsF_6^-\} \arrow[d, "NSF_3"] \\ & {[M(CO)_5NSF_3]^+AsF_6^-} \end{tikzcd} \tag{86}$$

$(M = Mn, Re)$

[In the meantime it has been shown that "pentacarbonyl hexafluoroarsenates" in the solid state have the structure $(CO)_5M\text{-}F\cdots AsF_5$; in their reactions, however, they behave as coordinatively unsaturated cations (*93*).]

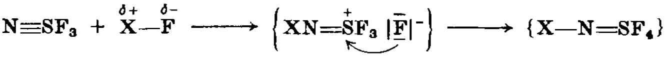
Reactions are better carried out in liquid $SO_2$, only a small excess of $NSF_3$ being necessary (*89*), e.g.,

$$C_5H_5Fe(CO)_2I + AgAsF_6 \xrightarrow[-AgI]{SO_2\ liq.} [C_5H_5Fe(CO)_2SO_2]^+AsF_6^- \xrightarrow[-SO_2]{+NSF_3} [C_5H_5Fe(CO)_2NSF_3]^+AsF_6^- \tag{86a}$$

Addition reactions with transition metal cations give an indication of the mechanism of additions to the $N{\equiv}S$ bond in $NSF_3$:

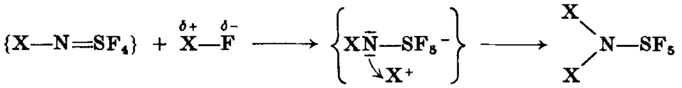
$$NSF_3 \begin{cases} + 2HF \longrightarrow SF_5NH_2 & (\mathit{25}) \\ + ClF \longrightarrow SF_5NCl_2 & (\mathit{28}) \end{cases} \tag{87}$$

Both reagents are highly polar $\left(\overset{\delta+}{H}—\overset{\delta-}{F};\ \overset{\delta+}{Cl}—\overset{\delta-}{F}\right)$, and in the first step the cation is added to nitrogen, following which this cation is neutralized by $F^-$:



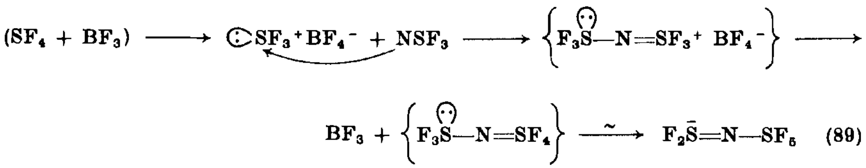
$$N{\equiv}SF_3 + \overset{\delta+}{X}—\overset{\delta-}{F} \longrightarrow \left\{XN{=}\overset{+}{S}F_3\ |\overline{F}|^-\right\} \longrightarrow \{X—N{=}SF_4\} \qquad (88)$$

The tetrafluorideimide adds a further X—F molecule. It seems more probable that a hexacoordinated anion is formed rather than a pentacoordinated cation.



(88a)

Compound $SF_5NSF_2$ is isolated in 3% yield from the reaction of $NSF_3$ with $SF_4$ in presence of $BF_3$ (*27*). Addition of the $\bar{S}F_3^+$ cation to nitrogen has been proposed as the primary step in the reaction mechanism:



$$(SF_4 + BF_3) \longrightarrow \overset{(\cdot\cdot)}{}SF_3^+BF_4^- + NSF_3 \longrightarrow \left\{F_3\overset{(\cdot\cdot)}{S}—N{=}SF_3^+\ BF_4^-\right\} \longrightarrow BF_3 + \left\{F_3\overset{(\cdot\cdot)}{S}—N{=}SF_4\right\} \xrightarrow{\sim} F_2\bar{S}{=}N—SF_5 \qquad (89)$$

The primary cation that would be expected is unstable under the reaction conditions. It takes $F^-$ from the anion to form neutral $F_3\bar{S}—N{=}SF_4$, a compound with 2 pentacoordinated sulfur atoms. Disproportionation then leads to $SF_5—N{=}\bar{S}F_2$, with 1 hexa- and 1 tetracoordinated sulfur. Equations (87)–(89) show that, outside of transition metal chemistry, there is evidence that iminosulfur trifluoride cations may be prepared by electrophilic attack on $NSF_3$. If the transition metal halide in Eq. (86) is replaced by HCl, it is possible to protonate the nitrogen (*94*):

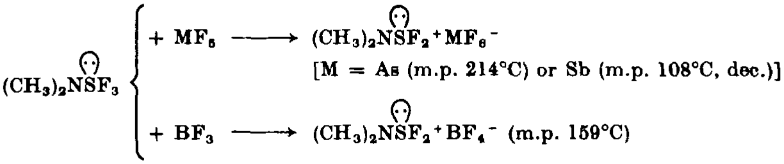
$$NSF_3 + HCl + AgAsF_6 \xrightarrow[-\,AgCl]{SO_2\ liq.} [HN{=}\overset{+}{S}F_3]\ AsF_6^- \qquad (90)$$

Isolation of pure $HNSF_3^+AsF_6^-$ was not possible, because some complexation of the silver occurs, and because two further stable compounds ($AsF_5 \cdot NSF_3$ and $SF_5NH_2 \cdot AsF_5$) are formed in the system $NSF_3/AsF_5/HF$.

### 3. *Derivatives of the* $\odot SF_3$ *Cation*

The $\odot SF_3^+$ ion is the analog in the chemistry of S(IV) of cations $O{=}SF_3^+$ or $RN{=}SF_3^+$ in that of S(VI). The only derivative described in the literature is $CF_3\underset{\odot}{S}F_2^+$ (*79a*); amino complexes may be prepared (a) by reactions of amino derivatives of $\odot SF_4$ with Lewis acids, (b) by cleavage of fluoride ions from a group bonded to tetracoordinated sulfur, and (c) by addition of cations to the nitrogen of a sulfur difluorideimide group.

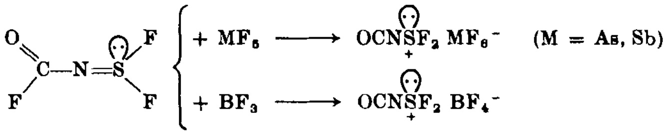
As for $OSF_4$, substitution of one or more fluorine atoms in $\odot SF_4$ by other groups, especially amino groups, brings about a very big increase in the ability of the molecule to act as a fluoride ion donor (*94*):



$$(CH_3)_2N\overset{\odot}{S}F_3 \begin{cases} + MF_5 \longrightarrow (CH_3)_2N\overset{\odot}{S}F_2{}^+MF_6{}^- \\ \quad [M = As\ (\text{m.p. } 214°C) \text{ or } Sb\ (\text{m.p. } 108°C,\ \text{dec.})] \\ + BF_3 \longrightarrow (CH_3)_2N\overset{\odot}{S}F_2{}^+BF_4{}^-\ (\text{m.p. } 159°C) \end{cases} \qquad (91)$$

In all cases, stable colorless high-melting solids are produced, which are readily soluble in $SO_2$ and are indefinitely stable in the solid state in dry glass vessels. Yields in the preparations are quantitative.

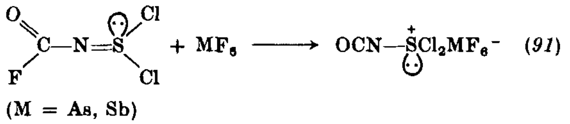
Reaction type (b) is illustrated by the *N*-fluoroformyl derivatives:



$$FC(O){-}N{=}\overset{\odot}{S}F_2 \begin{cases} + MF_5 \longrightarrow OCN\underset{+}{\overset{\odot}{S}}F_2\ MF_6{}^- \quad (M = As, Sb) \\ + BF_3 \longrightarrow OCN\underset{+}{\overset{\odot}{S}}F_2\ BF_4{}^- \end{cases} \qquad (92)$$

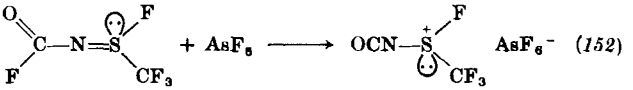
Whereas the hexafluoroarsenate and the antimonate are very stable, the tetrafluoroborate decomposes with loss of $BF_3$. On the basis of their vibrational spectra, the above compounds are not to be considered as acylium sulfur difluorideimide salts ($O\overset{+}{C}N{=}SF_2$).

Reaction (*92*) represents a general route to isocyanatosulfur cations:



$$FC(O){-}N{=}\overset{\odot}{S}Cl_2 + MF_5 \longrightarrow OCN{-}\underset{\odot}{\overset{+}{S}}Cl_2MF_6{}^- \ (91) \qquad (92a)$$

(M = As, Sb)



$$FC(O){-}N{=}\overset{\odot}{S}F(CF_3) + AsF_5 \longrightarrow OCN{-}\underset{\odot}{\overset{+}{S}}F(CF_3)\ AsF_6{}^- \ (152) \qquad (92b)$$

Additions to the S=N double bond of polar reagents are possible for the sulfur difluoride imides in the same way as for the triple bond in $NSF_3$, except that it is accompanied by cleavage of $SF_4$:

$$R{-}N{=}\overset{\odot}{S}F_2 + 2\overset{\delta+}{Cl^+}{-}\overset{\delta-}{F} \longrightarrow RNCl_2 + |SF_4 \quad (\mathit{35, 36}) \qquad (93)$$

$$R{-}N{=}\overset{\odot}{S}F_2 + 3\overset{\delta+}{H}{-}\overset{\delta-}{F} \longrightarrow RNH_3F + |SF_4 \quad (\mathit{94}) \qquad (93a)$$

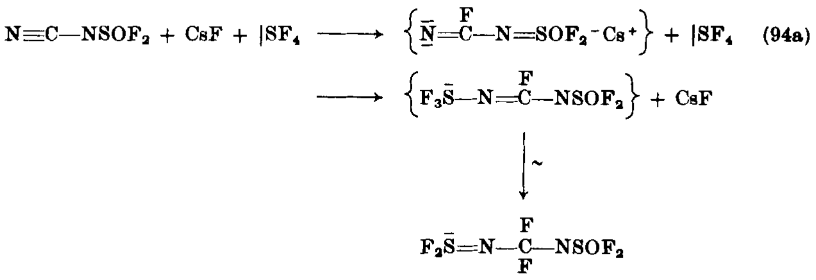
It must be assumed again here that the primary step involves addition of a cation to nitrogen. Under similar conditions, as was described for $RN{=}\overset{\overset{O}{\|}}{S}F_2$, it should be possible to trap the tetracoordinated nitrogen–sulfur cations.

## 4. *Reactions of Tetracoordinated Cations*

The characteristic of the cations is naturally their positive charge and they are, therefore, predestined for electrophilic attack or neutralization reactions with anions. Three possible types of reaction arise.

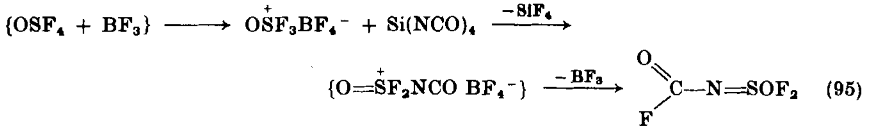
*a. Addition to Double Bonds or Reactions Resembling Friedel-Crafts Acylation.* Reactions of this sort have not been carried out in nitrogen–sulfur–fluorine chemistry. It has so far been necessary to proceed in the reverse way, increasing the nucleophilic character of the unsaturated reaction partner by anion formation, rather than increasing the electrophilic character of the N—S—F compound by cation formation, e.g.,

$$CF_3{-}CF{=}CF_2 + CsF + |SF_4 \longrightarrow \{(CF_3)_2\bar{C}F^-Cs^+\} + |SF_4 \quad (\mathit{130}) \qquad (94)$$
$$\longrightarrow (CF_3)_2CF\bar{S}F_3 + CsF$$



$$N{\equiv}C{-}NSOF_2 + CsF + |SF_4 \longrightarrow \left\{\bar{\underline{N}}{=}\overset{F}{C}{-}N{=}SOF_2{}^-Cs^+\right\} + |SF_4 \qquad (94a)$$
$$\longrightarrow \left\{F_3\bar{S}{-}N{=}\overset{F}{C}{-}NSOF_2\right\} + CsF$$
$$\big\downarrow \sim$$
$$F_2\bar{S}{=}N{-}\underset{F}{\overset{F}{C}}{-}NSOF_2$$

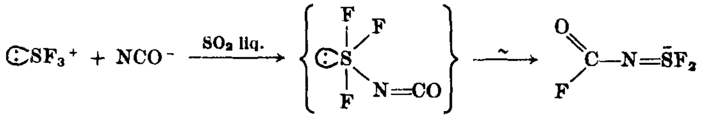
*b. Reactions with Nucleophiles.* The electrophilic character is so strongly enhanced by the positive charge on the central sulfur atom that even weak nucleophiles can be induced to react. The reaction of $\ominus SF_3{}^+BF_4{}^-$ with $NSF_3$ has already been described [Eq. (89)], and is of this type. $O{=}SF_4$ is appreciably less reactive than $\ominus SF_4$. Thus, whereas $Si(NCO)_4$ reacts with $\ominus SF_4$ even at room temperature, it is necessary with $OSF_4$ to use $BF_3$ as a catalyst and to heat to 235°–240°C (*134*):



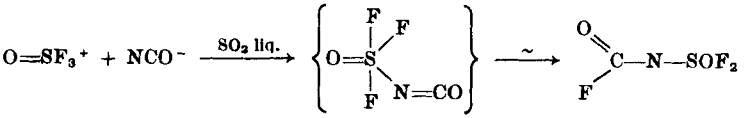
$$\{OSF_4 + BF_3\} \longrightarrow \overset{+}{O}SF_3BF_4{}^- + Si(NCO)_4 \xrightarrow{-SiF_4}$$
$$\{O{=}\overset{+}{S}F_2NCO\ BF_4{}^-\} \xrightarrow{-BF_3} \qquad (95)$$

*c. Reactions with Anions.* Although $:SF_3^+$ and $O{=}SF_3^+$ cations have been known for more than 15 years, there is no work in which their reactions as cations is described, e.g., reactions in which they interact with anions to form covalent molecules.

Using liquid $SO_2$ as solvent, both $:SF_3^+$ and $OSF_3^+$ will react with $NCO^-$ to yield the corresponding fluoroformylsulfur imides (*94*):



(96)



(96a)

These ionic reactions occur at very low temperatures under milder conditions than usual.

Using as the reaction principle the splitting off of a single fluorine followed by addition of an anion to form a new neutral compound, it is possible to exchange selected and, under mild conditions, single fluorine atoms. This will be illustrated by taking the haloformylsulfur imides as an example.

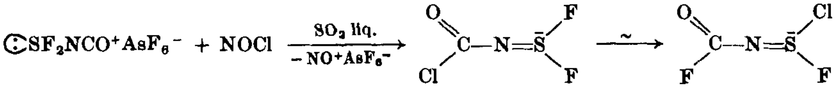
*N*-Fluoroformylsulfur difluorideimide may be prepared very readily from $Si(NCO)_4$ and $\bar{S}F_4$. With $PCl_5$ it is then possible first to exchange the fluorine atoms on sulfur and then that on carbon:

$$Si(NCO)_4 + 4\bar{S}F_4 \longrightarrow 4COFN\bar{S}F_2 + SiF_4 \quad (26) \qquad (97)$$

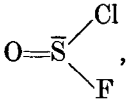
$$COFN\bar{S}F_2 + PCl_5 \xrightarrow{0^\circ} COFN\bar{S}Cl_2 + P(Cl,F)_5 \quad (128) \qquad (97a)$$

$$COFN\bar{S}Cl_2 + PCl_5 \xrightarrow{RT} COClN\bar{S}Cl_2 + P(Cl,F)_5 \quad (128) \qquad (97b)$$

In the reaction of $\bar{S}F_2NCO^+AsF_6^-$ with NOCl, on the other hand, the first step is not a nucleophilic attack of $Cl^-$ on sulfur, as the spectroscopic data would lead us to expect, but attack on the carbon of the isocyanate group (*92*):



(98)

The resulting $COClN\bar{S}F_2$ is unstable and rearranges to $COFN\bar{S}ClF$ which, in turn, dismutes at room temperature in an analogous way to , giving $COFN\bar{S}F_2$ and $COFN\bar{S}Cl_2$. Compound

$OSF_2NCO^+AsF_6^-$ reacts to give the more stable $COClNSOF_2$, and rearrangement to COFNSOClF is not observed:

$$OSF_2NCO^+\ AsF_6^- + NOCl \xrightarrow[-NOAsF_6]{SO_2\ liq.} COClNSOF_2 \qquad (98a)$$

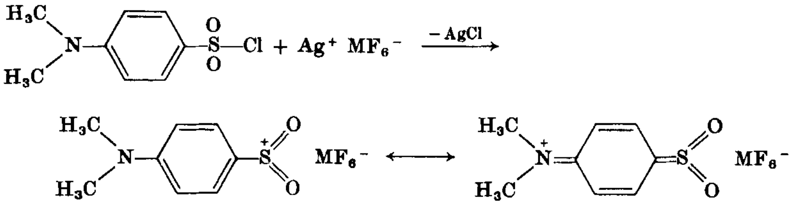
For exchange reactions of this sort, nitrosyl salts are in many cases particularly suitable as they are more soluble in $SO_2$ than the alkali salts. The nitrosyl compounds are often readily accessible by reaction of NOCl with the corresponding silver salts.

## B. THREEFOLD COORDINATED CATIONS

Whereas coordination number 3 occurs relatively frequently in the chemistry of quadrivalent sulfur (e.g., $O{=}\bar{S}{=}O$, $R{-}N{=}\bar{S}{=}O$, $R{-}N{=}\bar{S}{=}N{-}R$), it is seldom found for sulfur(VI). Apart from the monomer of $SO_3$, only very recently have some aza derivatives become known: $(R_3SiN{=})_3S$ (*66*); $(R_3SiN{=})_{3-x}(CF_3CON{=})_xS$ ($x = 1, 2$) (*74*); $(R_3SiN{=})_2S{=}O$ (*49*). This showed for the first time that the silylimino group is very suitable for stabilizing low coordination. In the meantime this principle has been used with great success in phosphorus chemistry (*107*), and the iminoaminophosphane, $R_3SiN{=}P{-}N\ (SiR_3)_2$ (*105*), and bis(imino)aminophosphorane, $(R_3SiN{=})_2P{-}N(SiR_3)_2$ (*106*), have proved to be key substances in a very large number of interesting reactions.

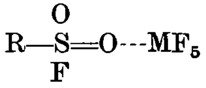
### 1. *Threefold Coordinated Cations of Sulfur*(VI)

Preparation of these cations is successful only in exceptional cases (*87*). The following reaction gave the desired sulfonylium salts, the hexafluoroantimonate of which is stable at room temperature (*88*):



(99)

The extraordinary stability of the *p*-amino compound was explained by supposing that the sulfur is able to transfer its positive charge to the aromatic group by forming quinoid limiting structures. If other sulfonyl compounds are used in reaction (99), either chlorine–fluorine exchange or rearrangement to donor–acceptor complexes of the type



$$R{-}\overset{\displaystyle O}{\underset{\displaystyle F}{S}}{=}O\cdots MF_5$$

takes place (*88*). Complexes of this sort are also encountered in the reaction of aminosulfonyl compounds, $R_2N\overset{O}{\underset{O}{S}}F$, with $SbF_5$ or $AsF_5$, and it is believed that the fluoride ion donor function is not greatly strengthened by the inductive effect of the amino group.

When one oxygen of sulfonyl fluoride, $O{=}\overset{F}{\underset{F}{S}}{=}O$, is replaced by a methylimino group, stable adducts are formed with Lewis acids (*94*):

$$R{-}N{=}S(O)F_2 + MF_5 \longrightarrow RN\overset{O}{\underset{F}{S}}F{\cdot}MF_5 \quad (M = As, Sb) \qquad (100)$$

It is not possible to make any definite prediction as to the nature of the coordination (cf. Section IV, A, 1).

## 2. *Threefold Coordinated Cations of Sulfur(IV)*

Whereas $O\bar{S}F_2$ does not form adducts of any sort with Lewis acids, replacement of 1 fluorine atom by a dialkylamino group leads to 1:1 adducts which, from NMR measurements, are formulated as salts (*94*):

$$R_2N{-}\overset{O}{\underset{(\cdot\cdot)}{S}}F + MF_5 \longrightarrow [R_2N{-}\overset{+}{\underset{(\cdot\cdot)}{S}}{=}O]\,MF_6^- \qquad (101)$$

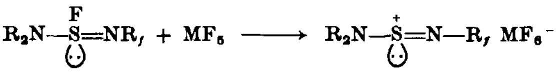
This class of compound is of interest because, as in the case of tetracoordinated S(IV) cations, the central sulfur atom does not violate the octet rule. The oxygen–sulfur bond may be described as a pure $p_\pi - p_\pi$ bond.

A second way of facilitating fluoride ion cleavage from the tetracoordinated fluoride is by replacement of the oxygen by an imino group (*94*):

$$CH_3N\bar{S}F_2 + AsF_5 \longrightarrow \text{decomposition} \qquad (102)$$

$$CF_3N\bar{S}F_2 + AsF_5 \longrightarrow \text{no reaction} \qquad (102a)$$

The primary adduct of $CH_3N\bar{S}F_2$ and $AsF_5$ decomposes at room temperature; the polyfluoroalkyl derivatives do not react. On substitution of 1 of the fluorine atoms by an amino group, salt formation again occurs, however (*94*):

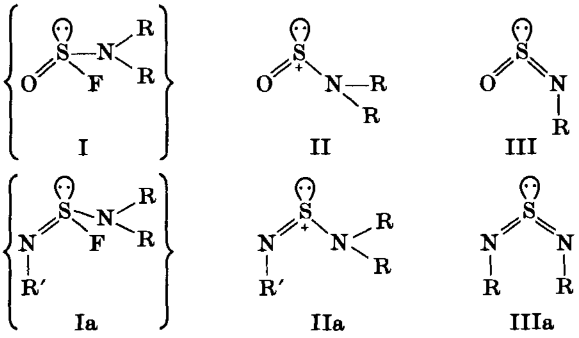


$$R_2N{-}\overset{F}{\underset{(\cdot\cdot)}{S}}{=}NR_f + MF_5 \longrightarrow R_2N{-}\overset{+}{\underset{(\cdot\cdot)}{S}}{=}N{-}R_f\ MF_6^- \qquad (102b)$$

Thus sulfur–nitrogen double bond may also be described as a pure $p_\pi - p_\pi$ bond.

In their bonding and structure the aminooxy- and aminoimino-

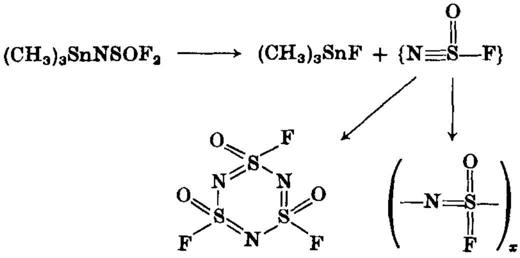
TABLE IV
RELATIONSHIP BETWEEN THREEFOLD COORDINATED NEUTRAL AND CATIONIC SULFUR(IV) SPECIES



sulfur(IV) cations are related to the thionyl imides and diimides (Table IV). Formally the diimides (IIIa) and thionylimides (III) contain two double bonds, and in the fluorides (I or Ia) there is one single and one double bond. In cations II or IIa, the positive charge on the central atom leads to strengthening of both bonds. Shortening of the single bond will occur in any case. Whether this is also detectable for the double bonds relative to thionyl imides or diimides must be settled by structural investigations (cf. Section VI).

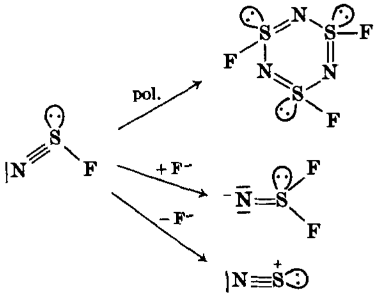
## C. DOUBLY COORDINATED CATIONS

From the discussion of threefold coordinated cations it is to be expected that it would be almost impossible to prepare doubly coordinated cations of sulfur(VI), for example "$\text{N}\equiv\overset{+}{\text{S}}=\text{O}$." The fluoride corresponding to this cation, "NSOF," would be expected as an intermediate in the decomposition of some sulfur oxydifluoride imides (*72*), e.g.,


(103)

but it stabilizes itself at once by increasing its coordination number.

Replacement of the doubly bonded oxygen by a free electron pair leads to $N{\equiv}\overset{:}{S}{-}F$, the analogous substance in the chemistry of sulfur(IV). This exists as a monomer and either polymerizes to the trimer or adds fluoride ions (increase in the coordination number). It can, however, also lose $F^-$ and go over to the thiazyl cation (*58*):



(104)

### 1. *Thiazyl Cation*, $N{\equiv}\overset{+}{S}\!:$

The thiazyl cation may be prepared from $N\bar{S}F$ and $MF_5$ at reduced pressure in the gas phase (*55*, *56*) or, on a preparative scale, in liquid $SO_2$ (*94*):

$$N{\equiv}\bar{S}F + MF_5 \longrightarrow N{\equiv}\overset{+}{S}\!:\,MF_6^- \qquad (M = As, Sb) \tag{105}$$

As in all of these reactions which result in salts or adduct formation, yields are almost quantitative. On vacuum sublimation the hexafluoro arsenate is obtained as colorless waxy solid which, in contrast to the very unstable $N\bar{S}F$, may be kept without decomposition for years in dry glass vessels. Thiazyl tetrafluoroborate (*62*, *63*) is stable only at low temperatures, decomposing completely at room temperature to $N\bar{S}F$ and $BF_3$.

So far there have been no structural investigations on thiazyl salts as it has not been possible to obtain single crystals. From the vibrational spectra it is apparent that there is a considerable strengthening of the N—S bond in relation to NSF (*55*, *56*).

Thiazyl salts are suitable for introducing N—S units into other molecules. Synthetic possibilities include reaction with anions, with nucleophiles, and with compounds having polar bonds. Their use in transition metal chemistry has also been suggested.

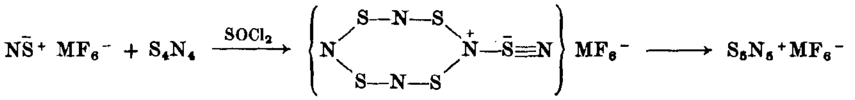
#### a. *Reactions with Anions* (*94*):

$$N\bar{S}^+AsF_6^- + NO^+CF_3SO_3^- \xrightarrow[-NO^+AsF_6^-]{SO_2\ liq.} N\bar{S}^+CF_3SO_3^- \qquad (m.p.\ 120°C) \tag{106}$$

The colorless and extremely hygroscopic salt may be separated from

$NO^+AsF_6^-$ by sublimation (30°C/0.01 torr). An ionic structure is assigned on the basis of the Raman spectrum.

*b. Reactions with Nucleophiles* (*94*):

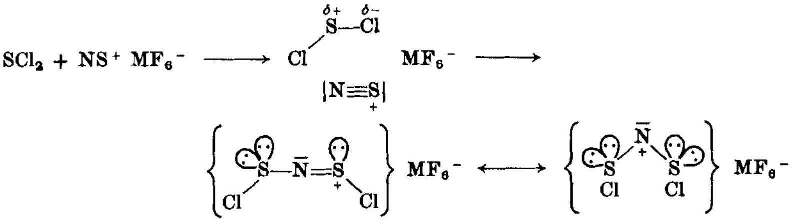


[M = As (yellow solid, m.p. 267°) or Sb (yellow solid, m.p. 175°)] (107)

The $N\overline{S}^+$ cation has been postulated (*4*) as an intermediate in the reaction of $N_3S_3Cl_3$ with $S_4N_4$ and $AlCl_3$, $FeCl_3$, or $SbCl_5$ in $SOCl_2$ as a solvent in the ratio 1:3:3. This mechanism seems to be supported by reaction (107). However, it is not possible to isolate $N\overline{S}^+SbCl_6^-$ from $(NSCl)_3$ and an excess, for example, of $SbCl_5$ in $SOCl_2$. Therefore, instead of the formation of $N\overline{S}^+$ it is possible that cyclic cations (cf. Section V, B) and their decomposition products are attacked nucleophilically by $S_4N_4$ in order to give the $S_5N_5$ salts.

The formulation of the intermediate in Eq. (107) is quite arbitrary because cycloaddition products of $N\equiv\overset{+}{S}\supset$ to $S_4N_4$ or linear cationic thiazenes would also be possible.

*c. Reactions with Polar Bonds* (*94*):



(108)

The $N(\underline{S}Cl)_2^+$ cation was first prepared from $NSF_3$ and $BCl_3$ as the tetrachloroborate (*57*). The more accessible tetrachloroaluminate is prepared (*67*) as follows:

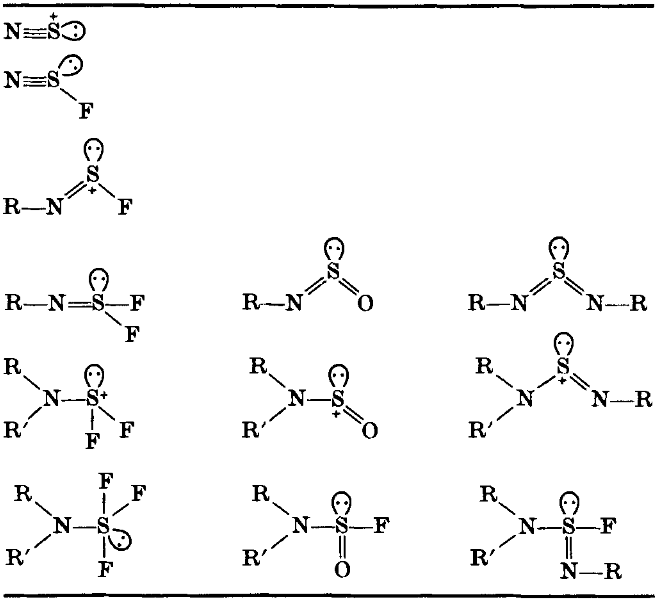
$$S_3N_3Cl_3 + 3\underline{S}Cl_2 + 3AlCl_3 \longrightarrow 3[N(\underline{S}Cl)_2]^+ AlCl_4^- \qquad (108a)$$

*d. Applications in Transition Metal Chemistry.* Reference has been made in the literature to the analogy between the $N\overline{S}^+$ cation and the lighter homolog $NO^+$ (*21, 29*), but preparation of the first thiazyl (thionitrosyl) complex was carried out in a completely different way (*21*):

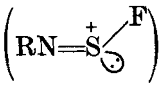
$$[MoN(S_2CNR_2)_3] + S_8 \xrightarrow[\text{reflux}]{CH_3CN} [MoNS\ (S_2CNR_2)_3] \qquad (109)$$

TABLE V

POSSIBLE NEUTRAL AND CATIONIC SPECIES IN ACYCLIC S(IV)–N CHEMISTRY



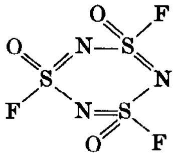
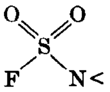
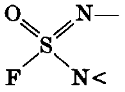
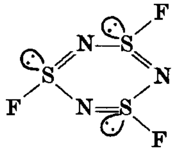
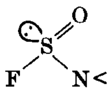
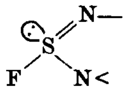
Since the $NO^+$ cation can be introduced directly into transition metal complexes through its salts (*30*), it should be possible for $N\bar{S}^+$ (*21*, *29*).

Table V shows the various possibilities for bonding sulfur(IV) and nitrogen. They range from a formal single bond to a triple bond strengthened by a positive charge. By variation of the group R and by forming cations and anions, it is possible to build up a continuous spectrum of bond types. In the chemistry of the anions, only $N\bar{S}F_2^-$ and $N\bar{S}O^-$ are so far known but, in the case of the cations, the last missing type of binding  $\left(RN{=}\overset{+}{S}{\lt}^{F}\right)$ has possibly been identified in $[Re(CO)_5NSF]^+$ (*89*).

## V. Cyclic Nitrogen–Sulfur–Fluorine Ions

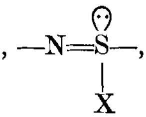
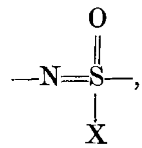
So far as coordination numbers are concerned, the chemistry of sulfur–nitrogen–halogen heterocycles (Table VI) is considerably simpler than that of the acyclic compounds, as sulfur is exclusively tetrahedrally coordinated. Other coordination numbers are rarely encountered among

TABLE VI
RELATIONSHIP BETWEEN CYCLIC AND ACYCLIC N—S—F COMPOUNDS

| | | |
|---|---|---|
|  |  |  |
| (Ia) | (Ib) | (Ic) |
|  |  |  |
| (IIa) | (IIb) | (IIc) |

the cyclic compounds of sulfur(VI), exceptions being the recently prepared disubstituted derivatives of $SF_6$ and $OSF_4$ (*1*, *168*). In the sulfanuryl (Ia) or thiazyl fluorides (IIa), there are steric relations similar to those in the acyclic fluorosulfonylamides (Ib) and fluorosulfinylamides (IIb) or their imino derivatives (Ic, IIc).

These heterocycles may be thought of as built up from acyclic units. Acyclic and cyclic systems are also very similar in their reactivity toward nucleophilic reagents. Aminosulfonyl fluorides may be prepared in aqueous solution from the sulfonyl chlorides by chlorine–fluorine exchange. Sulfinic acid amides react vigorously with water. Sulfanuryl fluorides are hydrolyzed only slowly, but thiazyl halides react spontaneously with destruction of the ring system.

Sterically, there is no great difference between a thiazyl,  $-\mathrm{N}{=}\underset{\underset{\textstyle X}{|}}{\mathrm{S}}-$, and a sulfanuryl group,  $-\mathrm{N}{=}\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle X}{|}}{\mathrm{S}}}-$, therefore they are interchangeable at will. The more sulfanuryl groups there are in a mixed ring, the greater is its stability.

Substitution reactions have been carried out successfully only on $(NSOF)_3$ (*58*, *101*) and $(NSOF)_2(N\bar{S}F)$ (*85*) [substitution taking place at S(IV)]. With pure thiazyl halides under the same conditions, one observes ring cleavage.

## A. CYCLIC ANIONS

Substitution reactions with sulfanuryl halides have been described in the literature (*58*, *101*), but only recently have careful systematic investigations led to a deeper understanding of them. From $(NSOF)_3$ and secondary amines, it is possible to obtain mono-, di-, or trisubstituted products by choice of conditions (solvent, stoichiometric proportions, temperature, reaction time) (*58*, *101*, *164*, *166*). By reaction with primary amines, hydrolysis, alcoholysis, or reduction, three different types of anion may be obtained: $(NSOF)_x(NSONR)_{3-x}^{(3-x)-}$ (*166*), $(NSOF)_2(NSO_2)^-$ (*162*), and $(NSOF)_2(NSO)^-$ (*162*).

### 1. *Aminosulfanuryl Fluoride Ions,* $(NSOF)_x(NSO\overline{\underline{N}}R)_{3-x}^{(3-x)-}$

In the reaction of $(NSOF)_3$ with primary amines, only 1 fluorine atom is exchanged initially (*166*):

$$(NSOF)_3 + 3RNH_2 \longrightarrow (NSOF)_2(NSONHR)\cdot RNH_2 + RNH_3F \qquad (110)$$

The substitution product is obtained as the amine adduct and is dissociated to ions in aqueous solution, giving difficultly soluble salts with $Ph_4AsCl$ and $Ph_4PCl$:

$$(NSOF)_2(NSONHR)\cdot RNH_2 \xrightarrow{H_2O} (NSOF)_2(NSO\overline{\underline{N}}R)^- + RNH_3{}^+ \xrightarrow[-RNH_3Cl]{Ph_4MCl}$$
$$Ph_4M^+\ (NSOF)_2(NSO\overline{\underline{N}}R)^- \qquad (111)$$

The free acid $(NSOF)_2(NSONHR)$ is produced by passing HCl into a suspension of the mixture from reaction (110) in ether:

$$(NSOF)_2(NSONHR)\cdot RNH_2 + HCl \longrightarrow (NSOF)_2(NSONHR) + RNH_3Cl \qquad (112)$$

Exchange of further fluorine atoms takes place only with great difficulty: The sulfanuryl ring in the amine adducts is present in the anionic form and nucleophilic exchange reactions with anions occur only under very vigorous conditions. Further exchange with primary amines has, indeed, been successfully carried out but results only in the trisubstituted product (*164*):

$$(NSOF)_2(NSONHR)\cdot RNH_2 + 3RNH_2 \longrightarrow (NSONHR)_3 + 2RNH_3F \qquad (113)$$

This is explained by the fact that the disubstituted product is less acidic and an amine adduct would have hardly any ionic character. As a result, exchange will occur substantially more readily than for the monosubstituted derivative. $(NSONHR)_3$ is devoid of acid character and amine adducts are not observed (*164*). If, on the other hand, one starts from the *N,N*-dialkyl derivatives the second fluorine atom can be exchanged and the product isolated (*164*):

$$(NSOF)_2(NSON(CH_3)_2) + 3RNH_2 \longrightarrow (NSOF)(NSONR_2)(NSONHR)\cdot RNH_2 + RNH_3F \qquad (114)$$

## 2. *Sulfanuric Fluoride–Sulfimide Ions*, $(NSOF)_{3-x}(NSO_2)_x^{x-}$

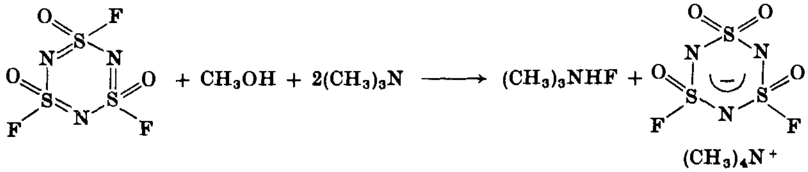
Although the trisulfimide is formed by hydrolysis of $(NSOCl)_3$ (*71*),

$$(NSOCl)_3 + 3H_2O + Ag^+ \text{ (excess) } \xrightarrow[-3AgCl]{} (AgNSO_2)_3\cdot 3H_2O \qquad (115)$$

it was reported in one of the first investigations on $(NSOF)_3$ that only one SF bond is cleaved on hydrolysis, the ring system remaining intact (*147*). This primary product may be isolated as a salt by using large cations (*162*):

$$(NSOF)_3 + HOH + Ph_4P^+ \longrightarrow (NSOF)_2(NSO_2)^-Ph_4P^+ + HF + H^+ \qquad (116)$$

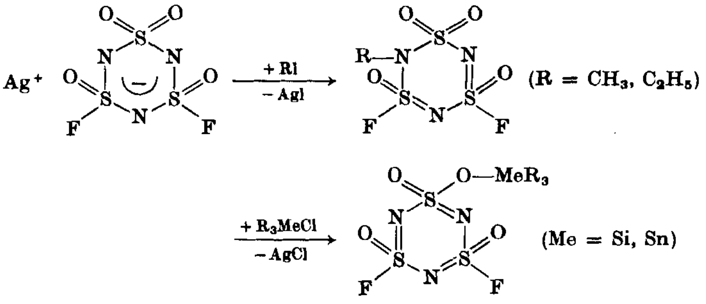
A more elegant route to this anion is afforded by reaction with methanol in presence of $(CH_3)_3N$ (*162*):



(117)

As with the acyclic derivatives, it seems that there is again a shift of the double bond to oxygen.

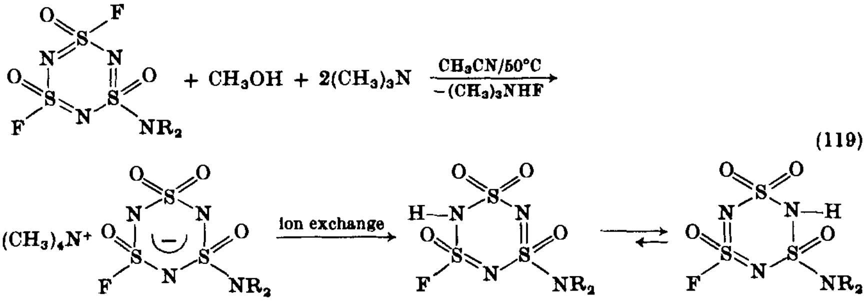
The tetramethylammonium salt is soluble in water without decomposition. Using an ion exchange resin, it is possible to isolate the free acid $(NSOF)_2(NHSO_2)$ as a hydrate. Reaction with silver carbonate yields the corresponding salt, which, in turn, may be used as a starting material for the preparation of mixed sulfanuryl fluoride–sulfimide derivatives (*163, 165*):



(118)

Alkylation occurs exclusively at the most nucleophilic site, whereas with trimethylchlorosilane or -stannane the thermodynamically favored oxygen derivative results. The first optically active inorganic ring was obtained with these alkysulfimide–sulfanuryl fluoride derivatives (*164*).

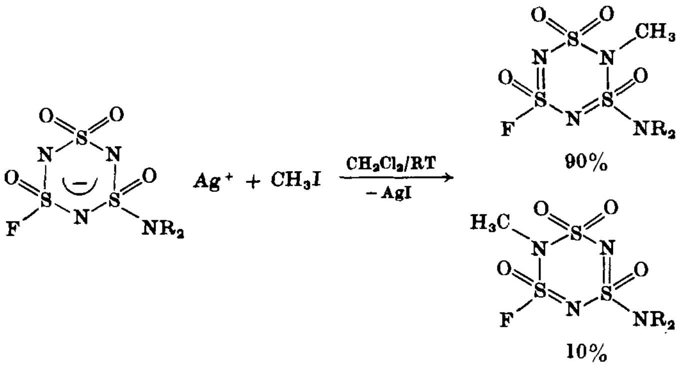
The foregoing reactions can also be carried out with sulfanuryl fluoride derivatives (*165*):



(119)

As would be expected, the amino derivatives are less acidic than $(NSOF)_2(SO_2NH)$, and they are less dissociated in aqueous solution. Since covalent compounds undergo nucleophilic attack more readily than anions, it is understandable that stability in aqueous solution increases with increasing acid strength.

As for $(NSOF)_2(HNSO_2)$, the silver salt may be prepared. On alkylation, both possible isomers are observed (*165*). Alkylation takes place, however, mainly at the most nucleophilic nitrogen.

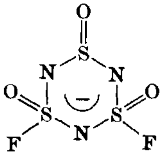


(120)

### 3. *Sulfanuryl Fluoride–Thionylimide Ions* $(NSOF)_2(NSO)^-$

If mercaptans are used instead of alcohols in the reaction shown in Eq. (117), the corresponding thio salt is not obtained. Instead, the sulfur that is attacked, undergoes reduction (*162*):

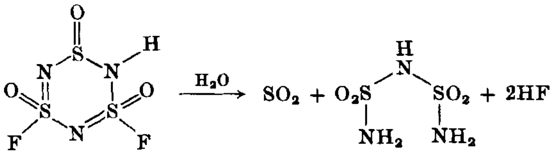
$(NSOF)_3 + 2CH_3SH + 2N(CH_3)_3 \longrightarrow$



$(CH_3)_3NH^+ + CH_3SSCH_3 + (CH_3)_3NHF$ (121)

This salt may also be prepared by reducing $(NSOF)_3$ with phenylhydrazine (*164*).

The free acid itself is not stable; cleavage of the ring occurs in aqueous solution, iminobissulfamide being formed (*164*):



(122)

Mixed thiazyl–sulfanuryl halides (*86*, *167*) may be obtained by reaction of the amino salt with $PCl_5$ or $PF_5$ (*164*):

$$(NSOF)_2NSO^-(CH_3)_3NH^+ \begin{cases} + PCl_5 \longrightarrow (NSOF)_2(NSCl) \\ \qquad\qquad\qquad (78\%) \\ + PF_5 \longrightarrow (NSOF)_2(NSF) \\ \qquad\qquad\qquad (5\%) \end{cases} \qquad (123)$$

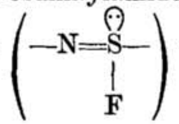
## B. Cyclic Cations

Until a short time ago the only known sulfur–nitrogen cation was $S_4N_3{}^+$ (*58*), but recently further species of this sort have been prepared; for example, as $S_5N_5{}^+$ (*4*, *6*, *7*, *125*), $S_3N_2{}^+$ or $S_6N_4{}^{2+}$ (*5*), and $S_3N_2{}^{2+}$ (*120*). The range of sulfur–nitrogen–halogen cations described in the literature is even more limited. The ionic structure of $S_3N_2Cl_2$ (Fig. 7) has been established by X-ray investigations (*169*). Examination of the bond distances shows the structure to be better described by II (derived from the threefold tetracoordinated ring system IIa) than by I (derived from a ring with sulfur in 3, 4, and 5, coordination). The different nature of the two chlorine atoms in $S_3N_2Cl_2$ is also apparent in its reactions, the ionically bound chlorine being exchanged under milder conditions than is covalent chlorine (*120*):

$$
S_3N_2Cl_2 \begin{cases}
+ XSO_3H \xrightarrow[RT]{CH_2Cl_2} S_3N_2Cl^+SO_3X^- + HCl \quad (X = Cl, F, CF_3) & (124) \\
+ 2XSO_3H \xrightarrow[reflux]{CH_2Cl_2} S_3N_2(SO_3X)_2 + 2HCl & (124a) \\
+ MCl_3 \xrightarrow[RT]{CH_2Cl_2} S_3N_2Cl^+MCl_4^- \quad (M = Fe, Al) & (124b) \\
+ SbCl_5 \xrightarrow[RT]{CH_2Cl_2} S_3N_2Cl^+SbCl_6^- & (124c) \\
+ 2SbCl_5 \xrightarrow[RT]{CH_2Cl_2} S_3N_2^{2+}\,(SbCl_6^-)_2 & (124d)
\end{cases}
$$

A fluorine compound with an analogous composition, $S_3N_2F_2$ (*65, 68*), has been reported in the literature. It has, however, been assigned the acyclic structure FS—N=S=N—SF; a closer study has yet to be made.

There are two possibilities for a systematic approach to the preparation of cyclic cations: (a) The corresponding chlorides may be reacted with $Ag^+MF_6^-$ (M = P, As, Sb), AgCl being split off to form the cation; or (b) as for the acyclic compounds, fluoride ions may be split off with Lewis acids.

As was discussed at the beginning of this chapter, sulfur is exclusively tetrahedrally coordinated in the halogenocyclothiazenes. Sulfur(VI) is chemically very similar to that in fluorosulfonylamides, and the sulfur(IV) to that in fluorosulfinylamides. We may, therefore, expect that only the thiazyl group  $\left(—N{=}\underset{\displaystyle F}{\underset{|}{S}}—\right)$ will function as a fluoride ion donor.

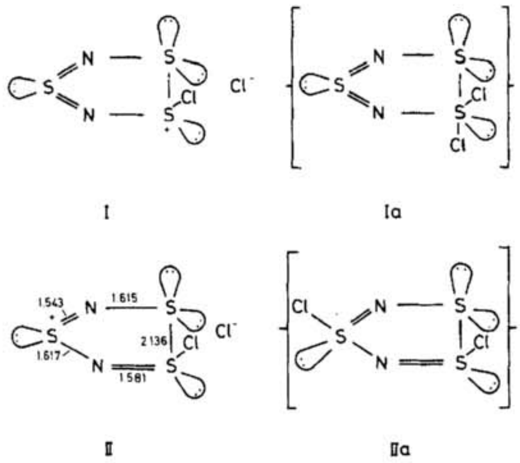
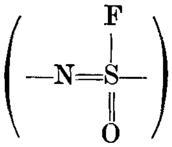


FIG. 7. Structure of $S_3N_2Cl^+Cl^-$.

The oxythiazene group  $\left(-N{=}\overset{F}{\underset{O}{S}}-\right)$ should either not react or coordinate through oxygen.

In the reaction of sulfanuryl fluoride with Lewis acids no stable adducts are observed, but with trithiazyl trifluoride salts are formed (*99*):

$$N_3S_3F_3 \begin{cases} + MF_5 \longrightarrow N_3S_3F_2^+ MF_6^- \quad (99) \quad (M = As, Sb) & (125) \\ + BF_3 \longrightarrow N_3S_3F_2^+ BF_4^- \quad (56, 99) & (125a) \end{cases}$$

The corresponding chloro cation [in $N_3S_3Cl_2^+SbCl_6^-$] may also be prepared. Both $N\bar{S}^+AsF_6^-$ and $N_3S_3F_2^+AsF_6^-$ are isolated by reaction of $(NSF)_4$ with excess $AsF_5$ (*99*):

$$\begin{tikzcd} N_4S_4F_4 + AsF_5 \arrow[r] & \{N_4S_4F_3^+AsF_6^-\} \arrow[r] & N\bar{S}^+AsF_6^- + N_3S_3F_3 \arrow[d, "AsF_5"] \\ & & N_3S_3F_2^+AsF_6^- \end{tikzcd} \qquad (126)$$

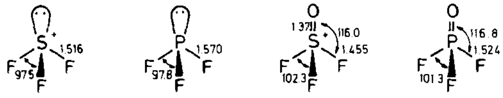
The $N_4S_4F_3^+$ cation is unstable and the eight-membered ring loses one NS unit. The remainder recombines to form the trimer rather than decompose (*99*).

These reactions show the $(NS)_3$ structure to be more stable than the tetramer, although $S_4N_4F_4$ is much less sensitive to hydrolysis. In the tetramer, nucleophilic attack on a ring sulfur atom is hardly possible because of the compact structure. With Lewis acids, however, reaction can occur on the ligands outside of the ring. Synthetic possibilities with these cations have not so far been examined in detail, but it is known that the reaction of $N_3S_3F_2^+AsF_6^-$ with NOCl gives only $(NSF)_3$ and $(NSCl)_3$ as isolable products (*94*).

It should be possible to prepare cations from the mixed thiazyl–sulfanuryl rings, $(NSOF)(NSF)_2$ (*167*) and $(NSOF)_2NSF$ (*86, 167*). Only the four-valent sulfur would, however, be capable of acting as a fluoride ion donor.

## VI. Relationship between Isoelectronic Sulfur and Phosphorus Compounds

Structural studies on $:SF_3^+$ (*47*) and $OSF_3^+$ cations (*81*) show that the molecular shape does not change in going from the cation to the isoelectronic neutral compound. This similarity in molecular shape of isoelectronic species has been fully discussed (*47*) and is attributed to



(47) (102) (81) (103)

FIG. 8. Isoelectronic sulfur and phosphorus fluorides and oxyfluorides.

orbital hybridization of the central atom, hybridization being characteristic of the periods of the periodic system to which the elements in question belong.

Since the shape of $\subset SF_3^+$ and $\subset PF_3$ or $OSF_3^+$ and $OPF_3$ (Fig. 8) is determined by the mutual influence of bonding and nonbonding electron pairs, it seems that the change of the effective nuclear charge of the central atom must have a similar effect on all electrons of the valence shell, whether they be bonding or nonbonding. For this reason the molecular shape of isoelectronic species will remain constant (*47*). If this is generally true, sulfur cations may be considered as model substances for the corresponding phosphorus compounds. Since they exist as solids at room temperature, structural studies on them are at present considerably simpler. Effects that occur at substantially lower temperatures with the phosphorus compounds are observable with the sulfur compounds in a readily accessible temperature range. Thus, for example, the NMR spectrum of $(CH_3)_2N\overline{S}F_2^+$ shows the molecule at $-15°C$ to have a semicoplanar structure (the atoms $SNC_2$ being in one plane that bisects the FSF angle) which is found for $(CH_3)_2N\overline{P}F_2$ in the solid state (*104*). Hindered rotation does not occur in the phosphorus compound down to $-90°C$. The high reactivity of low coordinated phosphorus compounds (*107*) and the restricted possibilities for their preparation render structural studies on these systems exceedingly difficult. The corresponding sulfur cations, $R_2N{-}\overset{+}{\underline{S}}{=}O$ or $R_2N{-}\overset{+}{\underline{S}}{=}N{-}R$, on the other hand, are very stable and are also readily accessible.

How far these structural similarities extend to chemical behavior has not yet been investigated, but it should be possible to carry over some of the reaction principles of phosphorus chemistry to the study of sulfur cations. One outstanding question is whether sulfur(IV) cations could function as ligands to transition metals in an analogous manner to phosphorus(III) compounds. Dialkylaminodifluoro cations would be especially suitable for such a study because of their high stability.

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