**Table VI.** Activation Parameters for Inversions at Asymmetric Nitrogen Centers in Metal Complexes

| complex | temp, °C | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, cu | ref |
|---|---|---|---|---|
| $[Co(NH_3)_4(sar)]^{2+}$ | 34.3 | 18.6 | 21 | 15 |
| $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ | 34.3 | 23.8 | 30 | 11 |
| *trans,trans*-$[Co(NO_2)_2(N\text{-Meen})_2]^+$ | 34.3 | 28.4 | 34 | 12 |
| $[Pt(N\text{-Meen})(NH_3)_2]^{2+}$ | 25.0 | 19.2 | 17 | 21 |
| $[Pt(N\text{-Meen})(phen)]^{2+}$ | 25.0 | 16.7 | 17 | 21 |
| *trans*-$[Co(dien)_2]^{3+}$ | 34.9 | 23.5 | 29 | 25 |
| *syn*-$[Co(trenen)N_3]^{2+}$ | 34 | 22.7 | 28 | 25 |

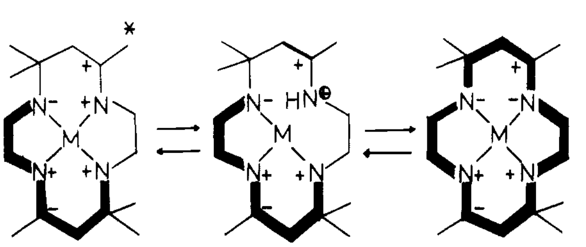
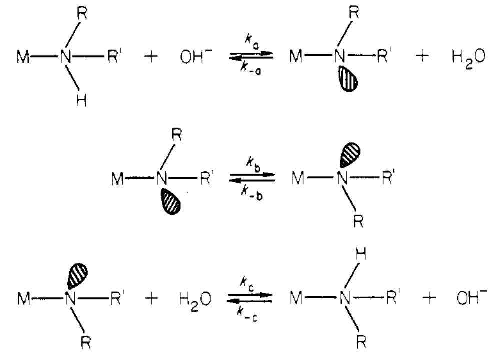


**Figure 9.** Configuration conversions of [Cu(tet a)(blue)]$^{2+}$ in strongly acidic media (key as in Figure 1).

exchanges and the nitrogen inversions of these complexes are consistent with the formation of a common intermediate as shown by eq 14–16.

Step 1 ($k_a$) leads to proton exchange. The rate constant of reprotonation ($k_{-a}$) is very large, much larger than the actual rate constant of inversion of the amide complex ($k_b$), resulting largely in retention of configuration. The activation parameters for the racemizations of these complex are listed in Table VI. The $\Delta S_2{}^{\ddagger}$ value for the free-base-catalyzed pathway of the blue-to-red interconversion of [Cu(tet a)(OH)]$^+$ is very similar to those listed in this table, suggesting the mechanism for the free-base-catalyzed pathway of the reaction of [Cu(tet a)(OH)(blue)]$^+$ is the same as that shown by this scheme (eq 14–16).



(14)

(15)

(16)

It is interesting to compare the $\Delta H^{\ddagger}$ values for the reactions of the open-chain-ligand complexes given in Table VI and that for the free-base reaction of [Cu(tet a)(OH)(blue)]$^+$. The racemization of each of these open-chain-ligand complexes needs to invert only one stable chelate ring; the $\Delta H^{\ddagger}$ values are in the range of 16.7–28.4 kcal/mol compared to a $\Delta H_2{}^{\ddagger}$ value of 22.8 kcal/mol for [Cu(tet a)(OH)(blue)]$^+$, which has to invert two adjacent unstable chelate rings.

There are three types of pathways for the blue-to-red interconversion of [Cu(tet a)]$^{2+}$ found under different conditions. In basic media, both coordinated-base-catalyzed and free-base-catalyzed pathways contribute to the observed rate. In strongly acidic media, this reaction is acid catalyzed due to the required cleavage of the copper–nitrogen bond.[5] This protonation pathway is shown in Figure 9.

**Acknowledgment.** We are grateful to the Chemistry Research Center, National Science Council of the Republic of China, for financial support. We are also grateful to the Chun-Sun Institute of Science and Technology of the Republic of China for elemental analyses and for providing laboratory facilities.

**Registry No.** OH⁻, 14280-30-9.

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# Some Reactions of Sulfonyl Hypohalites with Sulfur Tetrafluoride

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The reactions of $ClOSO_2F$, $BrOSO_2F$, and $ClOSO_2CF_3$ with $SF_4$ have been investigated. It has been found that the reactions proceed to form either trifluorosulfonium salts or covalent adducts. In the cases where the hypochlorites were used, the unusual cation $SF_4Cl^+$ can be postulated as a reactive intermediate. Characterizations of the new compounds $SF_3{}^+FSO_3{}^-$, $SF_3{}^+CF_3SO_3{}^-$, *cis*-$SF_4(Cl)OSO_2F$, *trans*-$SF_4(Cl)OSO_2F$, and *trans*-$SF_4(Cl)OSO_2CF_3$ are reported. The $SF_3{}^+$ salts are thermally unstable, decomposing to $SF_4$, $SOF_2$, and $(XSO_2)_2O$ (X = F, $CF_3$).

## Introduction

The sulfonyl hypohalites are a class of compounds whose great oxidizing power and electropholicity allow them to participate in a number of unique and interesting reactions.[1,2] For example, bromine(I) and Chlorine(I) fluorosulfate[2-4] and chlorine(I) and bromine(I) trifluoromethanesulfonate[4-6] have been shown to react with various covalent organic and inorganic halides to yield the corresponding sulfonic acid derivatives. These compounds have also been shown to add readily

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to electron-deficient olefins.[1,2,7,8] Chlorine(I) trifluoromethanesulfonate, in addition, undergoes oxidative addition to sulfur tetrafluoride.[4]

We wish to report the observation of new pathways for the reactions of chlorine(I) fluorosulfate, chlorine(I) trifluoromethanesulfonate, and bromine(I) fluorosulfate with sulfur tetrafluoride. In the cases where the hypochlorites were used, two pathways were evident. The first of these resulted in the formation of trifluorosulfonium sulfonate and pentafluorosulfur chloride, while the second led to the formation of covalent chlorotetrafluorosulfur sulfonates. Both of these processes may involve the chlorotetrafluorosulfur(VI)yl cation as an intermediate.

These observations contrast with those made by earlier workers,[9] who reported that, in the reactions of bromine(I) fluorosulfate and chlorine(I) fluorosulfate with sulfur tetrafluoride at 80 °C, only decomposition products were obtained. From our work, it is apparent that, at lower temperatures, these reactions proceed readily to provide some interesting new compounds.

## Experimental Section

**General Methods.** All volatile materials were handled in either a stainless-steel or a glass vacuum system equipped with stainless-steel or glass–Teflon valves, respectively. Pressures in the metal system were measured with a Heise Bourdon tube gauge, while those in the glass system were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Amounts of reactants and products were measured either by direct weighing or by *PVT* measurements, assuming ideal gas behavior. Temperatures were measured by a digital readout iron–constantan thermocouple.

Reactions were carried out in either Kel-F or FEP reaction vessels equipped with stainless-steel valves. After preliminary drying at 110 °C in an oven and then by evacuation, the vessels were dried by exposure to 200 torr of $SF_4$ for at least 30 min. In the cases where $BrOSO_2F$ or $ClOSO_2F$ was used as a reactant, the reaction vessels and short-path transfer system were pretreated with the equilibrium vapor of the hypohalite.

Infrared spectra were recorded on either a Perkin-Elmer Model 180 or Model 1330 spectrometer, using either a 10-cm glass cell or a 5-cm Monel cell, each fitted with AgCl windows. $^{19}F$ NMR spectra were recorded on a Varian XL-100-15 spectrometer, with $CFCl_3$ as the solvent and reference. Mass spectra were recorded on a Finnigan Model 4023-C mass spectrometer having chemical ionization and electron-impact sources. Raman spectra were recorded at −78 °C under dry nitrogen in a glass cell, with use of a Spex 14018 double monochromator with photon-counting detection and a Spectra Physics Model 164-03 argon ion laser for excitation.

**Reagents.** The compounds $ClOSO_2CF_3$,[5] $ClOSO_2F$,[10] and $BrOSO_2F$[11] were prepared by literature methods. Sulfur tetrafluoride was stored in a Monel cylinder over sulfur and was removed from the cylinder at −40 °C. $SF_4$ for reactions was measured in the metal system. Boron trifluoride and anhydrous HF were commercially available and were used as received.

**Preparation of $SF_3^+FSO_3^-$.** Chlorine(I) fluorosulfate (3.9 mmol) was transferred, under static vacuum, through a short glass connection, to a 10-mL FEP reaction vessel fitted with a stainless-steel valve and held at −196 °C. Sulfur tetrafluoride (15.6 mmol) was then condensed into the reactor, and the reactor was placed in an ethanol bath at −90 °C and allowed to warm to −40 °C over 4 h. At that point the reactor was cooled to −70 °C, and materials volatile at that temperature were transferred, under static vacuum, to a 75-mL stainless-steel cylinder (prepassivated with $F_2$) fitted with a stainless-steel valve and held at −196 °C. The reaction vessel was then warmed to −40 °C to ensure transfer of the residual volatile materials to the cylinder. After this operation, the reaction vessel was warmed to ca. 23 °C and held under dynamic vacuum for ca. 10 min. This left 0.29 g (1.5 mmol, 38% yield) of $SF_3^+FSO_3^-$ in the vessel.

$SF_3^+FSO_3^-$: white, finely crystalline, fibrous-appearing solid, slowly decomposing at 23 °C; Raman (solid, −78 °C) 1253 (m), 1084 (m), 930 (vw), 913 (s), 879 (s), 805 (w), 600 (w), 593 (w), 570 (w), 537 (w), 522 (vw), 417 (w), 413 (m), 408 (m), 196 (w), 161 (w), 88 (s), 63 (m), 46 (s), 32 (m) $cm^{-1}$.

The amount of $SF_5Cl$ present in the volatile materials from the reaction was determined as follows: The cylinder containing the volatile materials was cooled to −196 °C, and $BF_3$ (19 mmol) was added. The cylinder was then allowed to warm slowly to ca. 23 °C and left to stand overnight, in order to allow the reaction of $BF_3$ and $SF_4$, forming $SF_3^+BF_4^-$. At this point, the cylinder was cooled to −60 °C, and materials volatile at that temperature were collected in a trap held at −196 °C. Fractionation through −95, −135, and −196 °C traps gave $(FSO_2)_2O$ (0.72 mmol) in the −95 °C trap, a mixture of $SF_5Cl$ and $SOF_2$ (total 3.9 mmol) in the −135 °C trap, and $BF_3$ plus a small amount of $SF_5Cl$ (total 10.2 mmol) in the −196 °C trap. The total amount of $SF_5Cl$ present was calculated, from the average molecular weight of the −135 and −196 °C fractions, to be 3.0 mmol (77% yield based on $ClOSO_2F$).

**Thermal Decomposition of $SF_3^+FSO_3^-$.** Trifluorosulfonium fluorosulfate (0.21 g, 1.1 mmol), contained in an evacuated FEP reactor, was allowed to stand at 23 °C for 4 h. The effluent gases from the decomposition were collected in a trap held at −196 °C under dynamic vacuum. At the end of this period, final decomposition of $SF_3^+FSO_3^-$ was effected by heating with a hot-air gun.

The decomposition products were passed through −90 and −196 °C traps. Fluorosulfonic anhydride (0.68 mmol) collected in the −90 °C trap, while the −196 °C trap contained a mixture of $SF_4$, $SOF_2$, and a small amount of $SiF_4$ (total 0.76 mmol).

**Preparation of a Mixture of *cis*- and *trans*-$SF_4(Cl)OSO_2F$.** The reagents $ClOSO_2F$ (5.8 mmol) and $SF_4$ (23.2 mmol) were transferred to an FEP reaction vessel as described in the preparation of $SF_3^+FSO_3^-$. The vessel was then placed in a 0 °C bath. Two liquid phases formed within 5 min. The mixture was left at 0 °C for a further 1.5 h, at which time the vessel was cooled to −95 °C, causing precipitation of a white solid (probably $SF_3^+FSO_3^-$). Materials volatile from −95 to −70 °C were then pumped out of the reaction vessel and discarded.

The vessel was allowed to warm to room temperature while volatile materials were pumped into a trap held at −196 °C. A small amount of solid (0.20 g), presumably $SF_3^+FSO_3^-$, remained behind. The volatile maaterials were fractionated through −40, −90, and −196 °C traps. A tiny amount of viscous liquid collected at −40 °C and crude $SF_4(Cl)OSO_2F$ (3.1 mmol) at −90 °C. The material that collected at −196 °C consisted mainly of $SF_4$ and $SOF_2$ and was discarded. Refractionation of the crude $SF_4(Cl)OSO_2F$ through a −63 °C trap gave pure material (2.65 mmol, 46% yield).

$SF_4(Cl)OSO_2F$ (mixture of cis and trans isomers, 86% cis): colorless glass at −196 °C; mol wt found 240, calcd 242.5; IR 1485 (s), 1250 (s), 1025 (w, $SiF_4$), 905 (s), 880 (s), 860 (s), 830 (s), 810 (s), 740 (w, sh), 725 (m), 675 (m), 610 (m, sh), 580 (s), 560 (s), 525 (s), 460 (m) $cm^{-1}$; MS (CI), *m/e* (%) 183 (26.3), 153 (2.5), 145 (3.0), 143 (9.1), 129 (1.2), 115 (1.5), 109 (2.4), 107 (1.2), 105 (4.3), 103 (8.1), 101 (14.5), 99 (1.2), 91 (4.8), 89 (100.0), 87 (82.0), 85 (2.0), 83 (1.4), 71 (1.4); MS (EI), *m/e* (%) 182 (2.7), 167 (2.6), 165 (7.5), 163 (1.1), 145 (9.0), 143 (24.1), 133 (1.4), 127 (1.0), 126 (1.5), 121 (2.0), 114 (1.4), 108 (1.4), 107 (1.4), 105 (18.8), 103 (11.7), 101 (16.8), 100 (4.7), 99 (1.1), 95 (1.4), 89 (16.8), 88 (2.2), 87 (3.6), 86 (32.8), 85 (21.7), 83 (100.0), 81 (3.0), 80 (9.8), 76 (1.9), 72 (3.5).

*trans*-$SF^A{}_4(Cl)OSO_2F^B$: $^{19}F$ NMR $\delta$ 138.0 (doublet, $F^A$), 44.8 (quintet, $F^B$); $J_{AB} = 7$ Hz. *cis*-$F^A{}_2SF^B(Cl)F^C(OSO_2F^D)$: $^{19}F$ NMR $\delta$ 137.5 (complex triplet, $F^A$), 120.3 (complex quartet, $F^C$), 45.3 (multiplet, $F^D$); $J_{AB} = 152$, $J_{AC} = 158$, $J_{AD} = 8$, $J_{BC} = 146$, $J_{BD} = 1$, $J_{CD} = 8$ Hz. Small doublets appear at $\delta$ 49.0 and −144.2; splitting in each is 8 Hz. The singlet at $\delta$ 48.6 may be due to $SF_6$.

**$^{19}F$ NMR of *cis*- and *trans*-$SF_4(Cl)OSO_2CF_3$.** The preparation was carried out as described previously.[4]

*trans*-$SF^A{}_4(Cl)OSO_2CF^X{}_3$: $^{19}F$ NMR $\delta$ 143.6 (multiplet, $F^A$, overlaps $F^A$ of cis isomer), −73.6 (quintet, $F^X$, overlaps $F^X$ of cis isomer); $J_{AX} = 3$ Hz.

*cis*-$F^A{}_2SF^B(Cl)F^C(OSO_2CF^X{}_3)$: $^{19}F$ NMR $\delta$ 143.5 (complex triplet, $F^A$), 122.4 (complex quartet, $F^B$), 52.2 (complex quartet, $F^C$), −73.6 (multiplet, $F^X$); $J_{AB} = 152$, $J_{AC} = 158$, $J_{AX} = 3$, $J_{BC} = 146$, $J_{BX} = 0$, $J_{CX} = 4$ Hz.

**Reactions of $BrOSO_2F$ with $SF_4$.** In a typical reaction, $BrOSO_2F$ (2–6 mmol), a 4-fold molar excess of $SF_4$, and the appropriate amount

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of HF (when used) were condensed into either a Kel-F or an FEP reaction vessel at −196 °C. The vessel was then placed in a −70 °C bath and allowed to warm to −10 °C during 3–6 h. This treatment gave either a mixture of liquid and finely crystalline solid or two liquid phases.

In one case where a solid formed, the liquid phase was pumped off and the solid was allowed to decompose at room temperature under vacuum. An infrared spectrum of the decomposition products revealed the presence of $SF_4$, $SOF_2$, and $(FSO_2)_2O$.

In the cases where a liquid product formed, pumping for ca. 3–5 min at room temperature, after removal of excess $SF_4$, left a residue of nearly colorless, thermally unstable liquid. When allowed to decompose at ca. 23 °C, $SF_4$, $SOF_4$, and $(FSO_2)_2O$ were shown by IR analysis to be among the products. From the color, $Br_2$ and/or $BrOSO_2F$ were also formed. $^{19}F$ NMR gave no conclusive evidence for the structure of the product, due to problems with solubility and viscosity at temperatures where the material was stable.

**Preparation of $SF_3^+CF_3SO_3^-$.** Sulfur tetrafluoride (10.9 mmol) was condensed into an FEP reaction vessel containing $ClOSO_2CF_3$ (5.5 mmol) and held at −196 °C. The vessel was then placed in a dry ice–$CFCl_3$ bath at −78 °C and allowed to stand at that temperature for 1 h, during which time a crystalline solid formed. The vessel was then warmed to −40 °C, and materials volatile at that temperature were pumped into a Kel-F U-tube held at −196 °C. This left 1.09 g (4.6 mmol, 84% yield) of crystalline $SF_3^+CF_3SO_3^-$. The material was pale yellow, probably due to the presence of a small amount of unreacted $ClOSO_2CF_3$. The color was discharged (at the expense of decomposition of a significant portion of the salt) by brief warming to room temperature under dynamic vacuum.

An infrared spectrum of the volatile materials from the reaction showed the presence of $SF_5Cl$, $SOF_2$, and a small amount of $SiF_4$.

$SF_3^+CF_3SO_3^-$ decomposed at room temperature in a manner analogous to that of $SF_3^+FSO_3^-$, yielding $SF_4$, $SOF_2$, and $(CF_3SO_2)_2O$, as indicated by the IR spectrum.

$SF_3^+CF_3SO_3^-$: white crystalline solid, decomposing at 23 °C; Raman (solid, −78 °C) 1274 (s), 1224 (s), 1191 (w), 1173 (m), 1042 (s), 1036 (m), 930 (m), 918 (s), 884 (s), 773 (s), 592 (m), 580 (m), 543 (m), 520 (m), 517 (w), 428 (w), 417 (m), 356 (m), 352 (m), 327 (m), 193 (m), 136 (m), 120 (m) $cm^{-1}$.

## Results and Discussion

During the course of several preparations of $SF_4(Cl)OSO_2CF_3$ from $SF_4$ and $ClOSO_2CF_3$, it was observed that, at low temperatures, a considerable amount of a white crystalline solid formed. This material proved to be a trifluorosulfonium salt, $SF_3^+CF_3SO_3^-$.

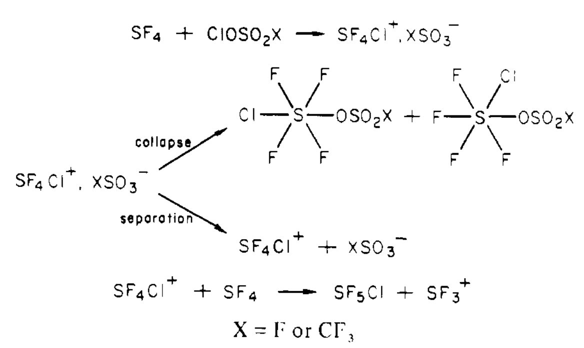
The observation of this facile low-temperature reaction of $ClOSO_2CF_3$ with $SF_4$ led to attempts to observe similar reactions using $ClOSO_2F$ or $BrOSO_2F$. In both cases, formation of $SF_3^+FSO_3^-$ was observed. In the case where $ClOSO_2F$ was used, reaction (evidenced by the formation of solids in the $SF_4$ phase) was evident as low as −90 °C.

The reaction of $BrOSO_2F$ with $SF_4$ was capricious. While the reactions of $ClOSO_2CF_3$ and $ClOSO_2F$ with $SF_4$ were readily reproducible and could be directed, by choice of the appropriate reaction conditions, toward either addition or $SF_3^+$ formation, this was not the case for the reaction of $BrOSO_2F$ with $SF_4$. This reaction, on three of eighteen occasions, produced $SF_3^+FSO_3^-$ (presumably, $SF_5Br$ was also produced; it was, however, not characterized), but the usual pathway led to formation of what appears to be a covalent adduct.

When the reaction mixtures were worked up, first by removal of materials volatile from −70 to −40 °C and then by holding the residue under dynamic vacuum at 23 °C, the less volatile liquid residue became nearly colorless. However, less than 1 min after a static vacuum was established, the liquid began to take on a dark orange-red color, possibly indicating the formation of $BrOSO_2F$ and/or $Br_2$. An infrared spectrum of the volatile decomposition products showed $SOF_4$, $SF_4$, and $(FSO_2)_2O$ to be present.

Attempts at characterization of the material by $^{19}F$ NMR were inconclusive. The material was only sparingly soluble in $CFCl_3$, $n\text{-}C_4F_9SO_2F$, or $(n\text{-}C_4F_9)_3N$ at −30 °C. It was soluble in $BrOSO_2F$ at that temperature, but rapid decomposition and/or reaction were observed by NMR, and no conclusive evidence for the structure of the material was obtained.

Scheme I



The reasons for the variation in the products of the reaction of $BrOSO_2F$ with $SF_4$ are not, at present, understood. Attempts at promotion of $SF_3^+FSO_3^-$ formation by the presence of small amounts of HF or $Br(OSO_2F)_3$, or by the use of HF as the solvent, were unsuccessful: in each of these cases, the liquid product was obtained, rather than $SF_3^+FSO_3^-$.

The reactions involving $ClOSO_2F$ and $ClOSO_2CF_3$ were more straightforward. The course of the reactions of either $ClOSO_2F$ or $ClOSO_2CF_3$ with $SF_4$ could be altered by varying the temperature of the reaction. For example, reaction of a mixture of $ClOSO_2CF_3$ with $SF_4$ at −78 °C for 1 h gave an 84% yield of $SF_3^+CF_3SO_3^-$; warming a similar mixture suddenly from −196 to 0 °C gave $SF_4(Cl)OSO_2CF_3$ in 45% yield (very little covalent adduct forms under milder conditions such as those under which $SF_3^+CF_3SO_3^-$ forms).

The mechanism for the formation of the products $SF_3^+XSO_3^-$ and $SF_5Cl$ or *cis*- and *trans*-$SF_4(Cl)OSO_2X$ (X = F, $CF_3$) is unclear, but we believe a logical explanation can be made by invoking the cation $SF_4Cl^+$ as an intermediate.[12] Initial attack of the highly electrophilic sulfonyl hypochlorites on $SF_4$ could give $SF_4Cl^+$ and $XSO_3^-$. The $SF_4Cl^+$ cation would then have two reactive pathways available to it: combination with $XSO_3^-$ to produce a covalent adduct or abstraction of fluoride from $SF_4$, forming $SF_5Cl$ and $SF_3^+$ (the same result would occur if $SF_4Cl^+$ reacted with $F^-$ produced by autoionization of $SF_4$). The dependence of the course of the reaction on the rate of warming may be due to an ion-pairing effect. The ion pair, $SF_4Cl^+,XSO_3^-$, may be relatively long-lived at low temperatures, allowing time for its dissociation to free ions. In that case, one would expect reaction of $SF_4Cl^+$ with $SF_4$ to predominate, since $SF_4$ is present in excess. On the other hand, rapid warming could cause the activation energy for combination of $SF_4Cl^+$ and $XSO_3^-$ to be reached rapidly, due to tighter association of the ion pair, thus promoting formation of the covalent adducts. In both reactions, a mixture of cis and trans isomers of $SF_4(Cl)OSO_2X$ is obtained, rather than only the cis isomer. These observations lend support to the proposal of $SF_4Cl^+$ as a reactive intermediate. Reaction of this cation (presumably of trigonal-biyramidal geometry) with a nucleophile could give either the cis or trans product depending on which face of the cation was attacked by the nucleophile. Concerted addition of $ClOSO_2X$

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(12) The $SF_5^+$ cation is well-known in the gas phase (Church, M. J.; Smith, D. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 137. Hitchcock, A. P.; Brion, C. E.; Van der Weil, M. J. *J. Phys. B* **1978**, *11*, 3245. Von Hellfeld, A.; Feldmann, D.; Welge, K. H.; Fournier, A. P. *Opt. Commun.* **1979**, *30*, 193), and $CH_3SF_4^+$ is obtained by reaction of $CH_3SF_5$ with $AsF_5$ and $SbF_5$. (Kleeman, G.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1037. Wessel, J.; Kleeman, G.; Seppelt, K. *Chem. Ber.* **1983**, *116*, 2399.)

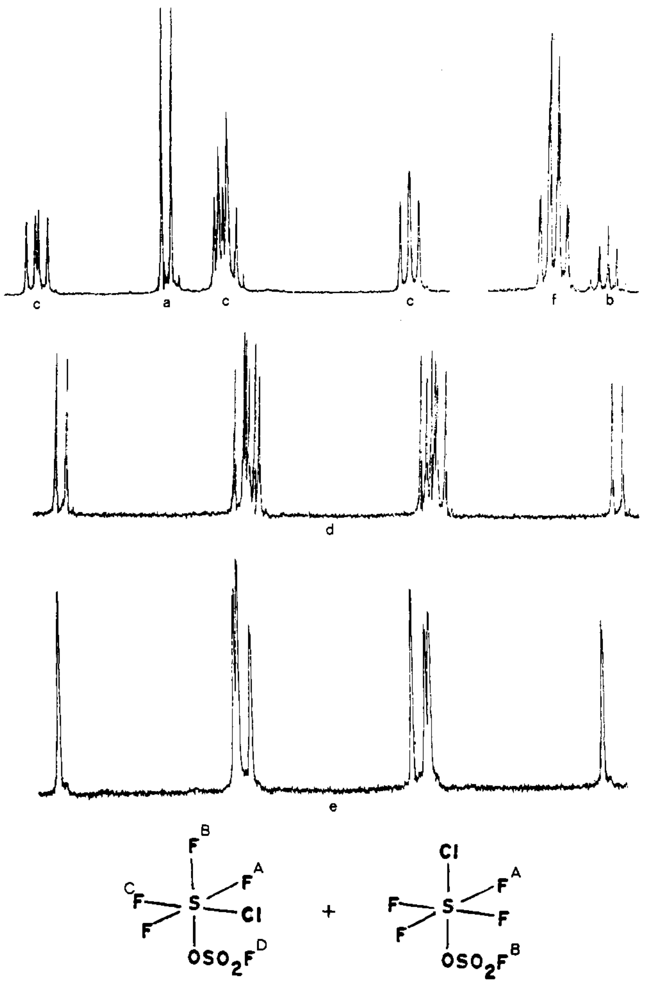

**Figure 1.** 94.1-MHz $^{19}$F NMR spectrum of a mixture of *cis*- and *trans*-SF$_4$(Cl)OSO$_2$F (86:14 cis:trans) at 500-Hz sweep width and 30 °C in CFCl$_3$: (a) F$^A$ of *trans*-SF$^A_4$(Cl)OSO$_2$F$^B$, $\delta$ 138.0, $J_{AB}$ = 7 Hz; (b) F$^B$ of *trans*-SF$^A_4$(Cl)OSO$_2$F$^B$, $\delta$ 44.8; (c) F$^A$ of *cis*-SF$_4$(Cl)OSO$_2$F, $\delta$ 137.5, $J_{AB}$ = 152 Hz, $J_{AC}$ = 158 Hz, $J_{AD}$ = 8 Hz; (d) F$^B$ of *cis*-SF$_4$(Cl)OSO$_2$F, $\delta$ 120.3, $J_{BC}$ = 146 Hz, $J_{BD}$ = 1 Hz; (e) F$^C$ of *cis*-SF$_4$(Cl)OSO$_2$F, $\delta$ 80.2, $J_{CD}$ = 8 Hz; (f) F$^D$ of *cis*-SF$_4$(Cl)OSO$_2$F, $\delta$ 45.3.

should, in contrast, give only the cis product[13] (see Scheme I[14]).

The structures of the covalent adducts were clear, from their $^{19}$F NMR spectra. While higher order splittings were present, the basic patterns of the NMR absorptions could be readily seen. This is illustrated by the spectrum of a mixture of *cis*- and *trans*-SF$_4$(Cl)OSO$_2$F (Figure 1). The spin system of the cis isomer is of the A$_2$BCD type. The complex quartet at $\delta$ 120.3 was assigned to F$^B$ of *cis*-SF$_4$(Cl)OSO$_2$F (see Figure 1) on the basis of the similarity of its chemical shift to that of the equatorial fluorines of SF$_5$Cl.[15] Consideration of the integrated intensities, multiplicities, and chemical shifts of the remaining absorptions led to their assignment as detailed in Figure 1. A computer-generated spectrum (Figure 2) showed a good agreement with the experimentally observed one. The NMR spectrum of *trans*-SF$_4$(Cl)OSO$_2$F appeared as a simple A$_4$B pattern.

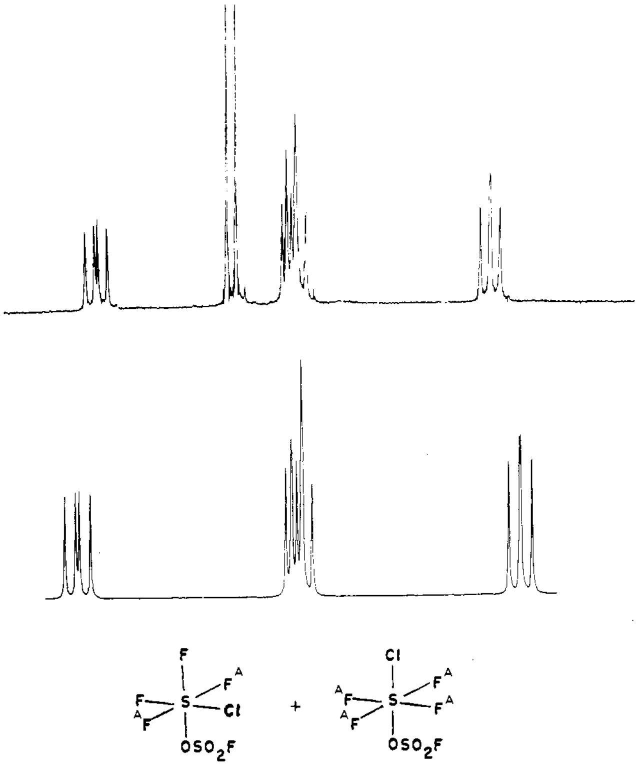

**Figure 2.** Upper trace: experimental 94.1-MHz $^{19}$F NMR spectrum of F$^A$'s of *cis*- and *trans*-SF$_4$(Cl)OSO$_2$F showing a doublet for the trans isomer and complex multiplets due to the cis isomer; sweep width 500 Hz. Lower trace: simulated spectrum showing transitions due to the F$^A$'s of *cis*-SF$_4$(Cl)OSO$_2$F.

Scheme II

$$\mathrm{SF_3{}^+XSO_3{}^- \rightleftharpoons XSO_2OSF_3}$$
$$\mathrm{XSO_2OSF_3 \rightleftharpoons XSO_2OSF_2{}^+ + F^-}$$
$$\mathrm{F^- + SF_3{}^+ \rightarrow SF_4}$$
$$\mathrm{XSO_2OSF_2{}^+ + XSO_3{}^- \rightleftharpoons (XSO_2O)_2SF_2}$$
$$\mathrm{(XSO_2O)_2SF_2 \rightarrow (XSO_2)_2O + SOF_2}$$
$$\mathrm{2SF_3{}^+XSO_3{}^- \rightarrow SF_4 + (XSO_2)_2O + SOF_2}$$
$$\mathrm{X = F \text{ or } CF_3}$$

The $^{19}$F NMR absorptions of a mixture of *cis*- and *trans*-SF$_4$(Cl)OSO$_2$CF$_3$ were also readily assigned. Assignment of the chemical shifts of *cis*-SF$_4$(Cl)OSO$_2$CF$_3$ were made on a basis similar to that used in making the assignments of those of *cis*-SF$_4$(Cl)OSO$_2$F. The spin system of the cis isomer is of the A$_2$BCX$_3$ type (again, good fit with the computer-generated spectrum). The spectrum of *trans*-SF$_4$(Cl)OSO$_2$CF$_3$, though badly overlapped by that of cis isomer, appeared to be a simple A$_4$X$_3$ pattern.

The SF$_3{}^+$ salts formed in these reactions turned out to be thermally unstable at room temperature, decomposing according to eq 1.

$$\mathrm{2SF_3{}^+XSO_3{}^- \rightarrow SF_4 + SOF_2 + (XSO_2)_2O} \qquad \mathrm{X = F \text{ or } CF_3} \tag{1}$$

The decomposition of each of the salts appeared to be accelerated by the presence of decomposition products: portions

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[13] Abe, T.; Shreeve, J. M. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 465.

[14] A reviewer suggested an alternative mechanism for the formation of SF$_5$Cl with ClOSO$_2$F:

$$\mathrm{SF_4 + ClOSO_2F \rightarrow \text{“}F_4S(Cl)OSO_2F\text{”} \rightarrow SF_5Cl + SO_3}$$

However, the analogous product with CF$_3$SO$_2$OCl would then be CF$_3$SF$_4$Cl and this is not observed. (CF$_3$SF$_4$Cl is well-known: Darragh, J. I.; Haran, G.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2289.) If SO$_3$ is an intermediate product in both reactions of XSO$_2$OCl (X = F, CF$_3$) with SF$_4$, there are no products that can account for the CF$_3$ group when X = CF$_3$. Finally, the covalent *cis*- and *trans*-SF$_4$(Cl)OSO$_2$X are stable at 22 °C and it is unreasonable to propose that some decomposition of these compounds can explain the observed results.

[15] Dungan, C. H.; Van Wazer, J. R. "Compilation of Reported F$^{19}$ Chemical Shifts 1951 to mid 1967"; Wiley-Interscience: New York, 1970.

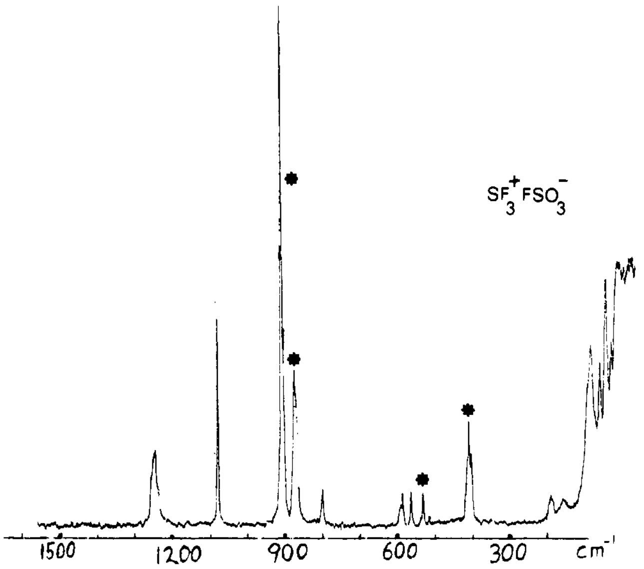

**Figure 3.** Raman spectrum of $SF_3^+FSO_3^-$ at −78 °C. Asterisks indicate bands assigned to $SF_3$.

of the salts sometimes liquefy during decomposition, and gas evolution from the liquefied material is rapid. The relatively low yield of $SF_3^+FSO_3^-$ (38%) may be due to a similar effect; apparently, this salt is less stable in solution than as a solid.

A possible mechanism for these decompositions involves a series of equilibria, the first of which would be a combination of the $SF_3^+$ and $XSO_3^-$ ions to form a covalent species, $XSO_2OSF_3$. This species could then reionize by a second path to form $XSO_2OSF_2^+$ and $F^-$. Combination of these ions with $XSO_3^-$ and $SF_3^+$, respectively, would produce $(XSO_2O)_2SF_2$ and $SF_4$. The species $(XSO_2O)_2SF_2$ would be expected to be unstable under the conditions, decomposing to $(XSO_2)_2O$ and $SOF_2$ in a manner observed for a number of covalent fluorosulfates.[1] The proposed decomposition is outlined in Scheme II.[16]

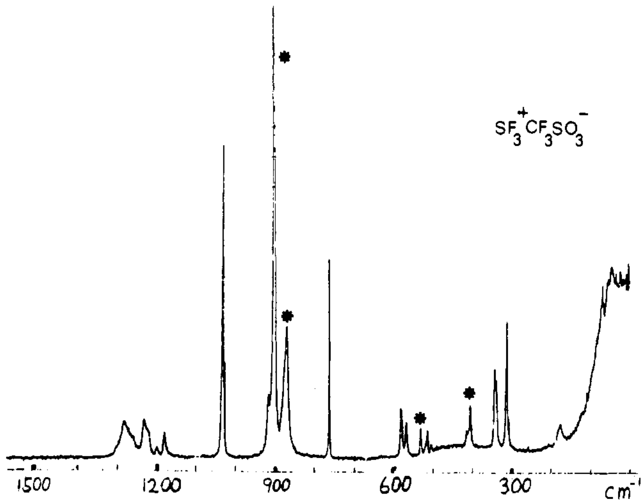

**Figure 4.** Raman spectrum of $SF_3^+CF_3SO_3^-$. Asterisks indicate bands assigned to $SF_3^+$. The broad feature from ca. 550 to 250 cm$^{-1}$ is probably due to fluorescence from a trace of $CF_3SO_3H$.

**Table I.** Comparison of the Positions of the Raman Bands (cm$^{-1}$) of $SF_3^+$ in Various Solid $SF_3^+$ Salts

| | compd | | | |
|---|---|---|---|---|
| vibration | $SF_3^+BF_4^-$ [c] | $SF_3^+AsF_6^-$ [c] | $SF_3^+FSO_3^-$ | $SF_3^+CF_3SO_3^-$ |
| $\nu_1$ [a] | 938 | 942 | 913 | 918 |
| $\nu_3$ [a] | 914 | 922 | 879 | 884 |
| $\nu_2$ [b] | 530 | 534 | 537 | 543 |
| $\nu_4$ [b] | 411 | 403 | 417 | 417 |

[a] Stretching modes. [b] Bending modes. [c] Reference 17.

The low-temperature (−78 °C) Raman spectra (Figures 3 and 4) of the solid materials confirm their formulation as $SF_3^+$ salts. The positions and intensities of the $SF_3^+$ bands are similar to those reported[17] for $SF_3^+BF_4^-$ and $SF_3^+AsF_6^-$ (see Table I), and the absorptions due to $FSO_3^-$ and $CF_3SO_3^-$ are very similar to those reported for other ionic fluorosulfates[18] and trifluoromethanesulfonates.[5] The shift of the S–F stretching modes to lower frequencies and the deformation modes to higher frequencies in $SF_3^+XSO_3^-$, relative to those in $SF_3^+AsF_6^-$ and $SF_3^+BF_4^-$, indicate anion–cation interactions and a degree of covalency for the $F_3S–OSO_2X$ bond.

**Acknowledgment.** The financial support of this research by the National Science Foundation is gratefully acknowledged.

**Registry No.** $SF_3^+FSO_3^-$, 88548-61-2; $SF_3^+CF_3SO_3^-$, 88548-63-4; *cis*-$SF_4(Cl)OSO_2F$, 88548-62-3; *trans*-$SF_4(Cl)OSO_2F$, 88588-20-9; *cis*-$SF_4(Cl)OSO_2CF_3$, 81439-33-0; *trans*-$SF_4(Cl)OSO_2CF_3$, 88588-21-0; $ClOSO_2F$, 13997-90-5; $BrOSO_2F$, 13997-93-8; $ClOSO_2CF_3$, 65597-24-2; $SF_4$, 7783-60-0; $SF_5Cl$, 13780-57-9.

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(16) A reviewer suggested the following reasonable decomposition for $SF_3^+FSO_3^-$:

$$2SF_3^+FSO_3^- \rightarrow 2SF_4 + 2SO_3$$

$$SF_4 + SO_3 \rightarrow SOF_2 + SO_2F_2$$

$$SO_2F_2 + SO_3 \rightarrow S_2O_5F_2$$

$$\text{net: } 2SF_3^+FSO_3^- \rightarrow SF_4 + SOF_2 + S_2O_5F_2$$

However, this cannot explain the analogous decomposition products for $SF_3^+CF_3SO_3^-$, which would require the formation of $CF_3SF_3$ (Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3058). No $CF_3S$ products are observed other than $(CF_3SO_2)_2O$. We have also checked the reaction of $SO_3$ with both $SO_2F_2$ and $SF_4$. $SO_2F_2$ does not react with $SO_3$ at 22 °C. With $SF_4$ at low temperature, $SF_3^+FSO_3^-$ is formed in high yield, and the salt decomposes at 22 °C to give the same products as found with $SF_3^+FSO_3^-$, formed from $SF_4$ and $FSO_2OCl$. (Note: This is a superior method of synthesis of $SF_3^+FSO_3^-$, and we shall present details for this reaction in the future.) Reaction of $SF_4$ and $SO_3$ at 22 °C gives the same products as the decomposition of $SF_3^+FSO_3^-$:

$$2SF_4 + 2SO_3 \rightarrow SOF_2 + S_2O_5F_2 + SF_4$$

(17) Gibler, D. D.; Adams, C. J.; Fischer, M.; Zalkin, A.; Bartlett, N. *Inorg. Chem.* **1972**, *11*, 2325.

(18) Tureshi, A. M.; Carter, H. A.; Aubke, F. *Can. J. Chem.* **1971**, *49*, 35.