A one-electron-transfer scheme suggests that the Marcus cross-reaction theory can be applied to the rate-determining step to determine whether it proceeds via an inner- or outer-sphere mechanism.[16] Some reactions of permanganate have been shown to be outer sphere by application of this theory.[11,17] There have been fewer studies of chlorine(III) reactions; however, a study of the kinetics of the reversible reaction between tris(1,10-phenanthroline)iron(III) and chlorine(III) was consistent with outer-sphere electron transfer.[18]

In Marcus theory, rate constants k_1 and k_2 are referred to as cross-reaction rate constants and are designated k_{12}. They can be calculated from eq 3. In this equation, k_{11} is the

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (3)$$

self-exchange rate constant for the Cl(IV)/Cl(III) couple ($\gtrsim 10^2$ M^{-1} s^{-1});[19] k_{22} is the corresponding rate constant for MnO_4^-/MnO_4^{2-} (4×10^3 M^{-1} s^{-1});[20] K_{12} is the equilibrium constant for the reaction; $\ln f_{12}$ and W_{12} can be calculated from self-exchange rate and equilibrium constants and from electrostatic work terms.[16] Dodgen and Taube established a lower limit on k_{11}, which they found to be essentially independent of $[H^+]$ in the pH range 0–5. The values of K_{12} for the two different reactions, permanganate–$HClO_2$ and permanganate–ClO_2^-, were calculated from the standard potential,[7] and our kinetically determined pK_a, with the assumption that equilibration $HClO_2^+ \rightleftharpoons H^+ + ClO_2$ is rapid. Then, with distances of closest approach 1.5 Å for ClO_2/ClO_2^-,[18] 3.3 Å for MnO_4^-/MnO_4^{2-},[15] and 2.4 Å for ClO_2^-/MnO_4^-, we calculate (at $[H^+] = 10^{-5}$ M) $k_1 = 0.34$ M^{-1} s^{-1} and (at $[H^+]$ = 1 M) $k_2 = 1.4 \times 10^{-2}$ M^{-1} s^{-1}. This calculation predicts values lower than those observed by factors of approximately 70 and 6600, respectively, and a trend in $[H^+]$ dependence opposite to that observed experimentally. It therefore seems likely that rate-limiting steps in the permanganate–chlorine(III) reaction proceed through an inner-sphere mechanism.

The stable[12] ions MnO_4^{2-} and MnO_4^{3-} are generated by feeding electrons into unoccupied antibonding orbitals on MnO_4^-.[21] Since at least a pair of electrons can be accepted, we picture the inner-sphere mechanism as taking place by attachment of a chlorine lone pair to manganese followed by electron transfer. Either permanganate or chlorite ions react as an ion pair, explaining the lack of ionic strength dependence. Only H^+ exerts a specific effect on the rate, acting as an accelerator, perhaps by stabilizing the active complex through H bonding between permanganate and chlorous acid oxygens.

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Registry No. MnO_4^-, 14333-13-2; ClO_2^-, 14998-27-7; $HClO_2$, 13898-47-0.

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Contribution from the Department of Chemistry,
Clemson University, Clemson, South Carolina 29631

Some Reactions of (Fluoroimido)tetrafluorosulfur[1]

BRIAN A. O'BRIEN and DARRYL D. DESMARTEAU*

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(Fluoroimido)tetrafluorosulfur undergoes a number of reactions with strong electrophiles, involving addition to the sulfur–nitrogen double bond. It also reacts readily with fluoride ion, forming the reactive nucleophile SF_5NF^-. Chlorine(I) fluorosulfate, bromine(I) fluorosulfate, and peroxydisulfuryl difluoride add to $F_4S{=}NF$, forming the respective cis adducts. The ^{19}F NMR spectra of these adducts provide the first examples of magnetic nonequivalence induced in an octahedral system by an adjacent chiral center. The anion SF_5NF^-, generated in situ from $F_4S{=}NF$ and KF, reacts readily with Br_2, forming SF_5NBrF, and with acyl fluorides, forming $RCONFSF_5$. The SF_5NF^- ion also reacts with $F_2C{=}NF$ to form $(SF_5NF)FC{=}NF$, which is isomerized to the unusual azo compound $F_5SN{=}NCF_3$ in the presence of CsF. Self-reaction of $F_4S{=}NF$ in the presence of KF does not produce the expected dimer $(SF_5NF)F_3S{=}NF$. Instead, extensive decomposition is observed, along with a low yield of the unusual amine $(SF_5)_2NF$.

Introduction

Compounds of sulfur, nitrogen, and fluorine containing multiple N–S bonds are well-known and have led to much unique and interesting chemistry. Among these compounds are examples containing triple (e.g., $N{\equiv}SF$, $N{\equiv}SF_3$, and $N{\equiv}SF_2(CH_3)$) and double (e.g., $F_4S{=}NR$, $(R)F_3S{=}NR$, $XX'F_2S{=}NR$, $XX'S({=}NR)_2$, $O_2S{=}NR$, and $(O)F_2S{=}NR$) bonds.[2] Despite the long and chemically productive history of this general class of compounds, reports of the synthesis and chemistry of imidotetrafluorosulfur compounds, $F_4S{=}NR$, have been few. Among the compounds of this class so far reported are $F_4S{=}NCF_3$,[3] $F_4S{=}NCH_3$,[4] and $F_4S{=}NSF_5$;[5] of these three compounds, extensive chemical investigations have been reported only for $F_4S{=}NSF_5$.[5] Some chemistry of a (perfluoroalkyl)(trifluoroimido)sulfur compound, $(CF_3)F_3S{=}NCF_3$,[6] has also been reported.

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Recently, the synthesis and characterization of the simplest fluorinated member of the series, $F_4S{=}NF$, (fluoroimido)tetrafluorosulfur, was reported.[7] Herein we wish to describe an investigation of some of the chemistry of this compound. (Fluoroimido)tetrafluorosulfur has been found to undergo reactions with acyl fluorides, perfluoromethanimine, bromine, and chlorine in the presence of KF. In addition, reaction of $F_4S{=}NF$ with $F_2C{=}NF$ in the presence of CsF leads to the azo compound $F_5SN{=}NCF_3$. These reactions are believed to proceed by way of the anion SF_5NF^-, formed by the reaction of $F_4S{=}NF$ with F^-. Ample precedent for the formation of SF_5NF^- may be found in mechanistically similar chemistry reported for $F_2C{=}NCF_3$,[8] $F_4S{=}NSF_5$,[5] $F_4S{=}O$,[9] and $F_2C{=}NF$.[10]

In another type of reaction, the strong electrophiles $XOSO_2F$ (X = Br, Cl, OSO_2F) have been found to add directly to the double bond of $F_4S{=}NF$, forming the unusual octahedral sulfur(VI) compounds *cis*-$SF_4(OSO_2F)NFX$. While many cis-disubstituted X_2SF_4 compounds have been reported,[11] in only a few instances have the two non-fluorine substituents been different. Specific examples of such compounds include $SF_4(OCF_3)OOCF_3$,[11b] $SF_4(NF_2)OCF_3$,[11c] $SF_4(Cl)OSO_2CF_3$,[11d,e] and $SF_4(Cl)OSO_2F$.[11e] In each of these specific cases, the reported ^{19}F NMR spectra have been complex, because the low symmetry of the molecules, due to the difference in the two substituents, increased the number of magnetically nonequivalent types of fluorine from two to three. In the new examples of cis-disubstituted $XX'SF_4$ compounds which we report here, an additional factor is present: the chirality of the NFX substituent. The proximity of this group to three of the four central fluorine atoms allows all four central fluorine atoms to become magnetically nonequivalent, giving rise to complex and highly characteristic ^{19}F NMR spectra.

Experimental Section

General Procedures. Volatile compounds were handled in either a stainless steel or a glass vacuum system fitted respectively with Teflon-packed stainless steel valves or with glass–Teflon valves. Pressures in the glass system were measured with a Wallace and Tiernan Series 1500 differential pressure gauge; those in the metal system were measured with a precision Heise Bourdon tube gauge. Temperatures were measured with a digital indicating iron–constantan thermocouple. Amounts of reactants and products were measured either by direct weighing or by PVT measurements, assuming ideal gas behavior.

Infrared spectra were recorded with a Perkin-Elmer Model 1330 spectrometer. A 10-cm glass cell fitted with AgCl windows was used. ^{19}F NMR spectra were recorded with a Varian XL-100-15 spectrometer, using ~80 mol % $CFCl_3$ as solvent and internal reference. High-field chemical shifts are negative. Mass spectra were obtained with a Finnigan 4021-C instrument at 70 eV for EI and CI (CH_4). Samples were introduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by the method of Kellogg and Cady[12] or by the use of a small isoteniscope.[13] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, chromatography was carried out on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 10 ft × $^3/_8$ in. or 2 ft × $^3/_8$ in. column packed with 35% halocarbon 11-21 polymer oil on acid-washed Chromasorb P was used.

Reagents. Chlorine, CF_3COF, CH_3COF, and C_2H_4 were obtained from commercial sources and were used as received. Active KF, CsF, RbF, and NaF–KF eutectic mixture[14] were prepared by fusion in a Pt dish, followed by grinding to fine powders in a dry mortar inside of a drybox. Carbonyl fluoride was prepared from $COCl_2$ and NaF in CH_3CN at 40 °C.[16] Perfluoropropionyl fluoride was prepared from the reaction of CF_3CF_2COCl with SbF_3/Cl_2. Bromine and $CFCl_3$ were dried by storage over P_4O_{10}.

((Fluorocarbonyl)imido)sulfur difluoride was prepared by a literature method,[15] except for the heating step, which was omitted. This modification led to the product in higher yield and in greater purity than were reported in ref 15. (Fluoroimido)tetrafluorosulfur was prepared as described previously,[7] with two exceptions: the $F_2S{=}NCOF$ was prepared as just described, and the dehydrofluorination of SF_5NHF to give $F_4S{=}NF$ was done with a NaF–KF eutectic (55% NaF by weight) mixture[14] rather than with KF. Reaction times, at −4 °C, varied from 15 min to ~5 h, depending on how many times the NaF–KF had been used previously. *Caution: On two occasions ~3-mmol samples of* $F_4S{=}NF$ *exploded with considerable force while they were warmed from −196 to +22 °C in a glass vessel. Due caution must be exercised in handling this compound and its derivatives, and sample size should be limited to 3 mmol.*

Peroxydisulfuryl difluoride,[17] $ClOSO_2F$,[18] $BrOSO_2F$,[19] and $F_2C{=}NF$[20] were prepared according to literature methods.

General Procedure for Reactions Involving Alkali-Metal Fluorides. Inside a drybox, the fused, finely powdered metal fluoride was placed in a one-piece ca. 120-mL Pyrex flask fitted with a glass–Teflon valve and containing a Teflon-coated magnetic stirring bar. After removal from the drybox and evacuation of the flask, the volatile reactant(s) were condensed into the flask at −196 °C, and the metal fluoride was stirred for an appropriate length of time at ca. 23 °C.

At the end of the reaction period, the volatile materials were separated by passage through a series of traps maintained at appropriate temperatures. Further purification by GLC was done in some cases.

Preparation of $SF_5N(F)COF$. Carbonyl fluoride (6.0 mmol) and $F_4S{=}NF$ (1.5 mmol) were condensed into a flask containing fused, powdered KF (1.36 g, 23.4 mmol), and the KF was stirred for 3 h at 23 °C. Fractionation (−111 and −196 °C) of the volatile materials

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by pumping on the sample container as it was warmed from −196 °C to the ambient temperature gave essentially pure $SF_5N(F)COF$ (1.4 mmol, 93% yield) in the −111 °C trap. The material was freed of minor impurities by GLC.

$F^ASF^B{}_4NF^XCOF^M$: bp 29 °C; mp −130 to −129 °C; mol wt 207.05 (calcd), 203.4 (found); log *P* (torr) = 5.939 − 410.2/*T* − 156 439.7/*T*^{2}; ΔH_{vap} = 6.60 kcal/mol; ΔS_{vap} = 21.8 eu; IR 1925 (sh, w), 1875 (C=O, s), 1810 (sh, w), 1250 (m), 1215 (m), 1070 (m), 1000 (m), 920 (s), 855 (s), 745 (w), 715 (w), 685 (m), 605 (s), 540 (sh, w); MS (CI) major *m/z* (%) 209 (1.4), 208 (MH^+, 100.0), 188 ($MH^+ - HF$, 5.8), 142 (SF_5NH^+, 1.2), 127 (SF_5^+, 31.8), 105 ($HNSF_3^+$, 1.2), 89 (SF_3^+, 15.4), 82 (4.5); MS (EI) major *m/z* (%) 129 (4.0), 127 (SF_5^+, 100.0), 108 (SF_4^+, 5.2), 91 (2.0), 89 (SF_3^+, 55.4), 85 (11.4), 70 (SF_2^+, 10.9), 69 (1.1), 51 (SF^+, 5.7), 47 (43.2), 46 (3.7), 44 (42.7), 42 (2.2); NMR A δ 58.4 or 57.7 (complex overlaps B), B 62.0 (complex), M −6.1 (d quintets), X −38.7 (br d) ($J_{AB} \simeq 150$ Hz, $J_{BM} = 14.0$ Hz, $J_{MX} = 60.0$ Hz).

Preparation of $SF_5N(F)COCF_3$. Trifluoroacetyl fluoride (12.5 mmol) and $F_4S{=}NF$ (2.5 mmol) were condensed into a flask containing fused, powdered KF (1.36 g, 23.4 mmol), and the mixture was stirred for 20 h at ca. 23 °C. Fractionation (−85 and −196 °C, while the sample container was warmed from −196 °C) gave essentially pure $SF_5N(F)COCF_3$ (1.3 mmol, 52% yield) in the −85 °C trap. Some noncondensable gas was formed in this reaction. The product was freed of minor impurities by GLC.

$F^ASF^B{}_4N(F^M)COCF^X{}_3$: bp 51 °C; log *P* (torr) = 6.490 − 724.4/*T* − 144 132.5/*T*^{2}; ΔH_{vap} = 7.39 kcal/mol; ΔS_{vap} = 22.8 eu; IR 1790 (s), 1750 (w, sh), 1315 (m), 1240 (s), 1190 (s), 1070 (s), 975 (w), 920 (s), 875 (s), 850 (sh), 815 (m), 730 (w), 695 (s), 645 (w), 605 (s), 585 (m), 525 (m) cm^{-1}; NMR A δ 58.0 (m), B 61.5 (m), M −53.7 (br s), X −73.4 (d), ($J_{AB} \simeq 150$ Hz, $J_{AM} \simeq 0$, J_{BM} = ?, $J_{MX} = 22$ Hz); MS (EI) major *m/z* (%) 141 (4.1), 127 (58.1, SF_5^+), 96 (25.6), 88 (47.7), 69 (100.0, CF_3^+); MS (CI) major *m/z* (%) 258 (100.0, MH^+), 162 (15.4, SF_5NHF^+), 142 (22.4); 127 (87.2, SF_5^+), 114 (17.2), 88 (41.7), 69 (29.1, CF_3^+).

Preparation of $SF_5N(F)COCF_2CF_3$. Perfluoroproprionyl fluoride (8.0 mmol) and $F_4S{=}NF$ (1.9 mmol) were condensed into a flask containing fused, powdered KF (1.36 g, 23.4 mmol), and the mixture was stirred for ca. 7 h at ca. 23 °C. Fractionation (−78 and −196 °C, while the sample container was warmed from −196 °C) gave essentially pure $SF_5N(F)COCF_2CF_3$ (0.72 mmol, 38% yield) in the −78 °C trap. Some noncondensable gas was observed in this reaction. The product was freed of trace impurities by GLC.

The use of only a fourfold excess of CF_3CF_2COF, relative to $F_4S{=}NF$, led to low yields (8–10%) of the product.

$F^ASF^B{}_4NF^MCOCF^X{}_2CF^Y{}_3$: mp −60.4 to −59.8 °C; IR 1775 (s), 1485 (w), 1350 (m), 1330 (m), 1275 (s), 1225 (s), 1205 (s), 1170 (s), 1120 (w), 1095 (m), 1020 (s), 925 (s), 870 (s), 830 (w), 785 (m), 740 (m), 690 (s), 605 (s), 585 (s), 565 (m), 535 (m) cm^{-1}; NMR A δ 57.8 (m), B 63.7 (m), M −52.8 (br s), X −119.6 (d-q), Y −82.3 (d-t) ($J_{AB} \simeq 150$ Hz, $J_{XY} \simeq 1$ Hz, $J_{MX} = 33$ Hz, $J_{MY} = 8.0$ Hz); MS (EI) major *m/e* (%) 147 (29.1, $C_2F_5CO^+$), 141 (3.2, SF_5N^+), 127 (90.5, SF_5^+), 119 (83.7), 108 (3.9), 100 (9.1), 89 (47.5, SF_3^+), 85 (11.6), 70 (12.2), 69 (100.0, CF_3^+), 50 (11.6, CF_2^+), 47 (19.5); MS (CI) major *m/z* (%) 308 (82.7, MH^+), 290 (5.8), 250 (5.9), 182 (12.6), 164 (14.0), 147 (19.5, $C_2F_5CO^+$), 142 (14.7, SF_5NH^+), 127 (78.71, SF_5^+), 119 (14.3), 104 (8.1), 89 (100.0, SF_3^+).

Preparation of $SF_5N(F)C(O)NSF_2$. ((Fluorocarbonyl)imido)sulfur difluoride (1.0 mmol) and $F_4S{=}NF$ (0.5 mmol) were condensed into a flask containing fused, powdered KF (0.65 g, 11 mmol), and stirring was begun. At the end of each of four successive ca. 20-min intervals, the volatile materials were fractionated (−40 and −195 °C), allowing removal of some of the product (−40 °C trap) before it could decompose completely. The materials from the −195 °C trap were then returned to the flask for further reaction. After the last cycle, a total of 0.0311 g (0.114 mmol, 22% yield) of product had been collected. the −195 °C trap as shown by IR to contain $F_2S{=}NCOF$ and $SF_5N(F)COF$.

$F^ASF^B{}_4NF^XCONSF^M{}_2$: colorless liquid at 23 °C; IR 1770 (s), 1435 (w), 1345 (sh), 1315 (s), 1255 (w), 1190 (w), 1185 (m), 1065 (w), 1015 (m), 915 (s), 885 (m), 850 (s), 765 (s), 750 (sh), 725 (s), 705 (sh), 605 (s), 555 (w), 485 (m) cm^{-1}; NMR A most intense peak δ 62.1 (m, partly overlaps B), B 62.6 (m), M 46.9 (br s), X −37.5 (br s), small impurity peaks 53.6 (s) and 52.1 (s); MS (EI) major *m/z* (%) 188 (3.0, SF_5NFCO^+), 129 (2.3), 127 (50.6, SF_5^+), 114 (4.8), 112 (100.0, F_2SNCO^+), 108 (2.3), 85 (12.7), 84 (4.4), 80 (2.0), 72 (2.3), 70 (50.6), 69 (9.0), 66 (2.5), 65 (12.2), 64 (20.1), 61 (2.5), 51 (13.2); MS (CI) major *m/z* (%) 273 (100.0, MH^+), 253 (3.4), 188 (2.2, SF_5NFCO^+), 162 (9.2), 142 (8.1), 132 (5.9), 127 (8.1, SF_5^+), 114 (4.4), 113 (2.0), 112 (72.0, F_2SNCO^+), 104 (3.0).

Attempted KF-Catalyzed Reactions of $F_4S{=}NF$ with $SF_5N(F)COF$ and with CH_3COF. When these reactions were attempted, under conditions similar to those just described, the $F_4S{=}NF$ was destroyed and the acyl fluorides were recovered unchanged.

KF-Catalyzed Self-Reaction of $F_4S{=}NF$. (Fluoroimido)tetrafluorosulfur (1.5 mmol) was condensed into a flask containing fused, powdered KF (5.57 g, 95.9 mmol), and the KF was stirred for ~20 h at ~23 °C. Fractionation (−78, −110, −196 °C) of the volatile materials gave crude $(SF_5)_2NF$ (0.17 mmol, ~23% conversion of $F_4S{=}NF$) in the −78 °C trap. The other traps contained mainly SF_4, SOF_2, SiF_4, and SF_6; noncondensable gas was also formed.

$(SF_5)_2NF$ was purified by GLC. The ^{19}F NMR, mass, and IR spectra of the material showed good agreement with those reported in ref 5.

Preparation of $SF_5N(F)CF{=}NF$. Unless purified by GLC, the $F_2C{=}NF$ prepared according to ref 20 usually contains CF_3COF as an impurity. This appears not to interfere significantly, since $F_2C{=}NF$ seems to be by far the more reactive of the two substances.

Perfluoromethanimine (1.6 mmol; containing some CF_3COF) and $F_4S{=}NF$ (1.7 mmol) were condensed into a flask containing fused, powdered KF, and the mixture was stirred for 135 min. Fractionation (−111 and −196 °C, while the sample container was warmed from −196 °C) of the volatile materials gave crude (containing, by IR, some CF_3COF) $SF_5N(F)CF{=}NF$ in the −111 °C trap. After further purification by GLC, 0.83 mmol (~50% yield) of $SF_5N(F)CF{=}NF$ was obtained.

In another, larger scale, GLC purification of $SF_5N(F)CF{=}NF$, a very minor component of high retention time was noted. Its infrared and mass spectra indicated that its structure was $[SF_5N(F)][CF_3N(F)]C{=}NF$.

$F^ASF^B{}_4NF^MCF^X{=}NF^N$: colorless glass, flows at −141 °C; IR 1670 (s, C=N), 1300 (s), 1060 (w), 1010 (m), 980 (s), 915 (s), 870 (s), 780 (m), 745 (w), 705 (w), 685 (m), 605 (s), 580 (m) cm^{-1}; MS (CI) *m/z* (%) 253 (2.0), 227 (4.5), 226 (1.4), 225 (MH^+, 83.0), 207 (1.2), 205 ($MH^+ - HF$, 9.9), 187 (1.2), 149 (2.4), 129 (4.5), 127 (SF_5^+, 100.0), 111 (2.1), 107 (4.1), 99 (2.5), 91 (1.9), 89 (SF_3^+, 42.8), 87 (1.8), 80 (1.03), 79 (40.4), 62 (5.1); (EI) *m/z* (%) 129 (4.4), 127 (SF_5^+, 100.0), 108 (SF_4^+, 4.4), 97 (19.9), 89 (SF_3^+, 71.9), 86 (1.1), 85 (21.5), 83 (1.2), 70 (SF_2^+, 19.2), 69 (1.3), 64 (11.5), 59 (6.0), 51 (7.4), 50 (4.0), 47 (1.6), 46 (3.7), 45 (4.4), 40 (3.4); NMR A complex most intense peak δ 56.8, B complex most intense peak 57.2, M −30.6 (br d), N −11.0 (br s), X −70.2 (br m) ($J_{MX} = 16$ Hz, other coupling constants not readily determined). $(SF_5NF)(CF_3NF)C{=}NF$: yellowish glass at −196 °C; IR 1670 (w, C=N), 1600 (w), 1490 (w), 1295 (s, sh), 1250 (s), 1195 (s), 1125 (m), 1020 (m), 975 (m, sh), 920 (s), 875 (m), 845 (m), 800 (w), 780 (m), 695 (m), 605 (m), 575 (m), cm^{-1}; MS (CI) *m/z* (%) 308 (MH^+, 9.1), 288 ($MH^+ - HF$, 3.4), 247 (1.4), 225 ($MH^+ - CF_3N$, 9.0), 210 (10.0), 208 (1.1), 192 (4.8), 162 (2.6), 152 (1.7), 151 (1.0), 149 ($MH^+ - SF_5N$, 21.7), 147 (3.6), 144 (1.0), 143 (7.5), 142 (SF_5NH^+, 14.5), 135 (1.5), 129 (4.9), 127 (SF_5^+, 53.9), 124 (3.1), 122 (SF_4N^+, 15.6), 114 (1.0), 109 (1.7), 107 (1.3), 105 (1.3), 104 (4.5), 103 (1.1), 102 (1.3), 101 (6.4), 99 (1.5), 89 (SF_3^+, 65.7), 87 (4.0), 85 (3.1), 84 (4.8), 79 (6.6), 74 (2.1), 70 (1.7), 69 (CF_3^+, 100.0), 67 (8.9), 66 (3.1), 65 (5.2), 62 (3.3); MS (EI) *m/z* (%) 149 (1.4), 137 (1.1), 135 (4.0), 129 (2.7), 127 (SF_5^+, 62.2), 119 (2.4), 114 (2.4), 108 (SF_4^+, 1.9), 100 (3.4), 97 (1.1), 92 (1.1), 91 (1.5), 89 (SF_3^+, 35.7), 87 (4.0), 86 (1.0), 85 (25.6), 83 (17.1), 76 (1.1), 70 (SF_2^+, 13.5), 69 (CF_3^+, 100.0), 67 (4.2), 66 (3.4), 65 (1.2), 64 (8.4), 59 (4.1), 54 (2.6), 51 (5.7), 50 (CF_2^+, 21.9), 48 (6.5), 47 (17.6), 46 (4.2), 45 (2.7), 44 (3.5), 43 (2.0), 40 (1.4).

Preparation of $F_5SN{=}NCF_3$. Perfluoromethanimine (1.4 mmol) and $F_4S{=}NF$ (1.4 mmol) were condensed into a flask containing fused, powdered CsF (3.20 g, 21.0 mmol), and the CsF was stirred at ca. 23 °C for 45 min. Trap-to-trap fractionation (−119, −196 °C) of the volatile materials gave $F_5SN{=}NCF_3$ (1.0 mmol, 71% yield) in the −119 °C trap. The material was freed of minor impurities by GLC.

$F^ASF^B{}_4N{=}NCF^X{}_3$: very pale yellow liquid, bp 16 °C; mp −124.3 to −123.8 °C; mol wt 224.06 (calcd) 221 (found); log *P* (torr) = 8.112 − 1534.0/*T* + 5874.5/*T*^{2}; ΔH_{vap} = 6.83 kcal/mol; ΔS_{vap} = 23.6 eu; IR 1600 (m, −N=N−), 1245 (s), 1190 (s), 1160 (sh), 890 (s), 875 (w), 825 (w), 785 (w), 610 (m), 580 (m), 565 (sh) cm^{-1}; MS (CI) *m/z* (%) 225 (MH^+, 7.2), 127 (SF_5^+, 2.4), 104 ($HNSF_3^+$, 5.0), 91

(1.9), 89 (SF_3^+, 41.5), 77 (1.4), 70 (SF_2^+, 2.7), 69 (CF_3^+, 100.0), 67 (5.3); MS (EI) *m/z* (%) 127 (SF_5^+, 17.3), 108 (SF_4^+, 2.0), 91 (1.6), 89 (SF_3^+, 38.4), 86 (1.1), 70 (SF_2^+, 11.7), 69 (CF_3^+, 100.0), 64 (1.0), 51 (6.6), 50 (CF_2^+, 25.5), 48 (1.1), 47 (2.2), 46 (2.9), 44 (4.8); NMR A δ 56.0 (m), B 38.5 (m), X −71.6 (s) ($J_{AB} \simeq 150$ Hz).

Isomerization of $SF_5N(F)CF{=}NF$. Exposure of $SF_5N(F)CF{=}NF$ (0.31 mmol) to stirred, fused, powdered CsF (0.67 g, 4.4 mmol) for 25 min yielded $F_5SN{=}NCF_3$ quantitatively.

A similar experiment with fused, powdered RbF (0.42 g, 4.0 mmol) and $SF_5N(F)CF{=}NF$ (0.46 mmol) for ca. 19 h, with periodic checking by IR, produced only a small amount of isomerization, with $F_5SN{=}NCF_3$ being the only observable product.

Preparation of SF_5NBrF and SF_5NClF. (Fluoroimido)tetrafluorosulfur (0.50 mmol) and bromine (0.50 mmol) were condensed into a flask containing fused, powdered KF (5.6 g, 96 mmol), and the KF was stirred for ~3 h at ~25 °C. Fractionation of the volatile materials through −85, −126, and −196 °C traps gave SF_5NBrF, somewhat contaminated with Br_2, in the −85 °C trap, with the a smaller amount being collected at −126 °C. Some noncondensable gas was formed, and no $F_4S{=}NF$ remained. The crude yield of SF_5NBrF was 80%.

In a similar manner, SF_5NClF[7] was prepared, in 48% yield, from $F_4S{=}NF$, Cl_2, and KF.

It was found that the Br_2 could be removed from the product by brief exposure to an excess of ethylene, followed by fractionation (−50, −85, −196 °C traps). 1,2-Dibromoethane was collected at −50 °C, while SF_5NBrF was collected at −85 °C.

$F^ASF^B_4NBrF^X$: mol wt 239.96 (calcd), 236 (found); IR 920 (vs), 860 (s), 780 (w), 725 (m), 690 (m), 600 (s), 580 (sh); NMR A δ 52.4 (m), B 47.1 (m), X 46.1 (br s) ($J_{AB} = 145$ Hz, other coupling constants not readily determined).

Reaction of $F_4S{=}NF$ with $ClOSO_2F$. Chlorine(I) fluorosulfate (1.6 mmol) was transferred through a short glass connection, and under static vacuum, to an FEP tube (ca. 20-mL volume) equipped with a stainless steel valve and held at −196 °C. (Fluoroimido)tetrafluorosulfur (1.7 mmol) was then condensed into the reactor (in some places on the walls of the vessel, a brief flash of brown-red color was seen). The reactor was then placed in a −30 °C bath. The reaction mixture was held at −30 °C for 10 min and then warmed to room temperature. Trap-to-trap fractionation (−40, −196 °C) of the resulting light yellow liquid gave 0.35 mmol of colorless liquid, which was shown by NMR (see Results and Discussion) to consist of a 65:15:20 mixture of *cis*-$SF_4(OSO_2F)FCl$, *cis*-$SF_4(OSO_2F)_2$, and *trans*-$SF_4(OSO_2F)_2$. *cis*-$SF_4(OSO_2F)NFCl$ appeared to be thermally unstable near 24 °C, decomposing with moderate rapidity, with concomitant formation of a yellow gas, presumably Cl_2.

Preparation of *cis*-$SF_4(OSO_2F)NFBr$. Bromine(I) fluorosulfate (0.6 mmol) was transferred through a short glass connection, under static vacuum, to a ca. 120-mL glass reactor held at −196 °C. All parts of the system were treated with the equilibrium vapor of $BrOSO_2F$ before the transfer was made. The transferred $BrOSO_2F$ was then allowed to melt and distributed as a thin film in the flask. The film was then frozen at −196 °C, and $F_4S{=}NF$ (0.6 mmol) was condensed into the flask. The flask was then placed in an ethanol bath in a Dewar flask, at −100 °C, and left to gradually warm. The contents of the flask showed marked discoloration by the time the temperature reached −90 °C. After 6.5 h, the temperature had reached −45 °C, and the flask contents had become dark brown-violet, for the most part. Further warming, in the air, caused disappearance of this color. The colorless liquid that formed began to decompose fairly rapidly at room temperature, with concomitant formation of a brown-orange vapor (presumably Br_2). Trap-to-trap fractionation (−30, −196 °C) gave a colorless liquid in the −30 °C trap. This material released Br_2 when handled in the vacuum system and appeared to have an equilibrium vapor pressure of ca. 5 torr. An NMR sample was prepared by transfer of the material, under static vacuum, through a short glass connection, to an NMR tube maintained at −196 °C. The sample was then warmed to ca. −30 °C, and volatile impurities were pumped away over 30 min. Fluorotrichloromethane was then added at −196 °C. See Results and Discussion for details of the NMR spectrum.

Preparation of *cis*-$SF_4(OSO_2F)NF(OSO_2F)$. Peroxydisulfuryl difluoride (1.0 mmol) and $F_4S{=}NF$ (1.0 mmol) were condensed into a ca. 120-mL Pyrex flask equipped with a glass–Teflon valve and held at −196 °C. The flask was then left to warm in the air (~23 °C). (*Caution*: More rapid warming, with use of a water bath, once resulted in a minor explosion.) The reaction mixture was then left at ~23 °C for 1.5 h. Fractionation (−40, −80, −196 °C) gave 0.24 g (0.71 mmol, 71% yield) of *cis*-$SF_4(OSO_2F)NF(OSO_2F)$ in the −40 °C trap. Some noncondensable gas was present, and a small amount of FSO_2OOSO_2F collected in the −80 °C trap. The −196 °C trap contained (by IR) mostly $(FSO_2)_2O$. Some FSO_2OOSO_2F and SiF_4 were also present.

cis-$SF_4(OSO_2F)NF(OSO_2F)$: colorless glass at −196 °C; equilibrium vapor pressure at 23 °C 6 torr; IR 1490 (s, OSO_2F), 1250 (s, OSO_2F), 1025 (w), 990 (m), 925 (s), 890 (s), 870 (s), 810 (s), 745 (w), 695 (m), 680 (m), 650 (w), 615 (sh, w), 580 (s), 550 (s), 455 (w). See Results and Discussion for details of the NMR spectrum.

Results and Discussion

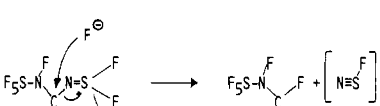
Fluoride-Catalyzed Reactions of $F_4S{=}NF$ with Acyl Fluorides. The reactions of certain acyl fluorides with $F_4S{=}NF$ in the presence of KF lead to acylated amidopentafluorosulfur derivatives, $SF_5N(F)COR$. The formation of these products is best explained by invoking the ion SF_5NF^-, formed from $F_4S{=}NF$ and F^-, as an intermediate. Acylation of this ion would lead to the observed products. These processes are illustrated in eq 1 and 2. The yield of acylated

$$F_4S{=}NF + F^- \rightarrow \underset{\mathbf{1}}{F_5S{-}NF^-} \tag{1}$$

$$F_5S{-}NF^- + RCOF \rightarrow F_5S{-}N(F)COR + F^- \tag{2}$$

product is markedly dependent on the nature of the R group. Increasing the size of R or decreasing its electronegativity led to drastic decreases in the yields of products. Thus, a yield of ~90% was obtained for R = F; changing R to CF_3 or CF_3CF_2, under similar conditions, led to yields of acylated products of 53% and 8%, respectively. (The yield of $SF_5N(F)COCF_2CF_3$ could be increased, however, by using a large excess of CF_3CF_2COF.) No acylated product was obtained when R was CH_3 or SF_5NF. Also, since $F_4S{=}NF$ readily decomposes in the presence of active KF, there is, in all of these reactions, a competition between destruction of $F_4S{=}NF$ and acylation of the anion derived from it, leading to low yields of acylated products when the less reactive acyl fluorides are used.

In the case where R = $F_2S{=}NCO$, a third process was found to be operating, namely, catalytic destruction of the acylated product by KF. This process is illustrated in reaction 3. The acyl fluoride $F_2S{=}NCOF$ is known to decompose in



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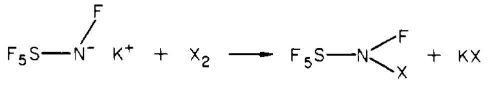
(3)

an analogous manner in the presence of CsF,[15] so the observed destruction of $SF_5N(F)CONSF_2$ by active KF is not particularly surprising. A 22% yield of **2** was obtained by fractionation of the reaction mixture at short intervals; this procedure removed a substantial amount of **2** before it could react further.

The pentafluoro(fluoroamido)sulfur compounds are all stable, volatile, colorless liquids at room temperature. They were characterized by their mass, infrared, and ^{19}F NMR spectra and by their physical properties.

Oxidation of SF_5NF^- by Br_2 and Cl_2. The ion SF_5NF^-, generated from $F_4S{=}NF$ and KF, was found to react readily with Br_2 or Cl_2, forming respectively SF_5NBrF (**4**) and SF_5NClF (**5**) as illustrated in eq 4. This behavior is analogous



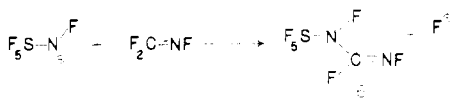
$$F_5S{-}N^-(F)\;K^+ + X_2 \longrightarrow F_5S{-}N(F)X + KX \tag{4}$$

X = Br (**4**), Cl (**5**)

to that reported for the ion CF_3NF^-.[10] Compound **5** has been reported previously,[7] but this constitutes the first synthesis of SF_5NBrF.

Compound **4** is a pale greenish yellow liquid that is only moderately stable at room temperature. It can be handled in a glass vacuum system for short periods, but it appears to be photosensitive, decomposing upon extensive handling, with release of Br_2, as evidenced by the color that develops.

Fluoride-Catalyzed Reactions of $F_4S{=}NF$ with $F_2C{=}NF$. Perfluoromethanimine was found to undergo a facile reaction with SF_5NF^- (generated from $F_4S{=}NF$ and KF), leading to compound **6**. Compound **6**, a stable, colorless liquid, was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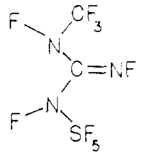
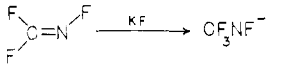
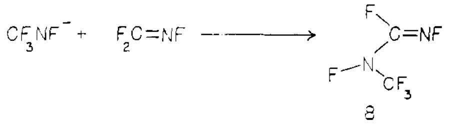
characterized by its IR, ^{19}F NMR, and mass spectra. In addition to **6**, a very small amount of a heavier product was isolated. Infrared and mass spectral evidence suggested that its structure is **7**, but further characterization was precluded


7

by the small amount of material. An ion at m/z 308 (2.1%), corresponding to MH^+, was observed in the chemical ionization mass spectrum, with no heavier ions of significant intensity being detected. Ions of high relative abundance were also detected at *m/z* 127 (SF_5^+, 53.9%) and 69 (CF_3^+, 100.0%). The infrared spectrum of the material, in addition to major absorptions attributable to C–F stretching vibrations and S(VI)–F vibrations, contained a band at 1670 cm^{-1} attributable to a C=N stretch. Compound **7** could arise by nucleophilic attack of CF_3NF^- (from $F_2C{=}NF + F^-$) on the primary product **6**. The lack of reactivity of **6** with SF_5NF^- is not unexpected, since the structurally similar $SF_5N(F)COF$ was also unreactive. Presumably the smaller CF_3NF^- is, for steric reasons, better able to attack **6**. An alternative explanation for the formation of **7** is attack by SF_5NF^- on $(CF_3NF)F$-$C{=}NF$ (**8**) (see below).

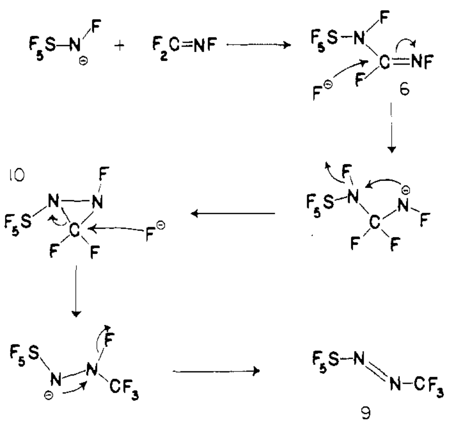
It was interesting to find that no important competing reactions occurred in this system. For instance, self-reaction of $F_2C{=}NF$ over active KF leads smoothly to the formation of a dimer,[10] as illustrated in eq 6 and 7. There was no indication


(6)


(7)

that this process was occurring efficiently, even though CF_3NF^- must have been present. The results of the experiment may be rationalized in either of two ways: (1) SF_5NF^- is, in the absence of overriding steric factors, a much more reactive nucleophile than CF_3NF^-, being rapidly trapped by either $F_2C{=}NF$ (leading to **6**) or $(CF_3NF)FC{=}NF$ (**8**) (leading to **7**); (2) $F_4S{=}NF$ is more reactive than is $F_2C{=}NF$, thus favoring formation of SF_5NF^- over CF_3NF^-. Other reactions that were possible, but not observed, were fluoride-promoted destruction of $F_4S{=}NF$ and displacements by CF_3NF^- on $F_4S{=}NF$.

Scheme I



In surprising contrast to the behavior noted for the reaction of $F_4S{=}NF$ with $F_2C{=}NF$ in the presence of active KF, it was found that the same reaction in the presence of active CsF led, not to compound **6**, but to the unusual azo compound **9**. We propose the mechanism outlined in Scheme I to explain the formation of **9**. The initial step is essentially identical with that observed for the case where KF was used as the catalyst: displacement of F^- from $F_2C{=}NF$ by SF_5NF^-, forming **6**. The more active CsF is able to further isomerize **6** to diaziridine **10**. This postulate is supported by the fact that the analogous compound from the dimerization of $F_2C{=}NF$, **8**, is readily isomerized by active CsF to the corresponding diaziridine, which in turn could be quantitatively isomerized to $CF_3N{=}NCF_3$ with Fe, Cr, or Ni metal. In the case described here, however, it appears that diaziridine **10** is unstable to further rearrangement, suffering ring opening followed by loss of F^-, yielding azo compound **9**.

Strong support for the intermediacy of **6** in the formation of **9** was obtained in a separate experiment. Exposure of a sample of **6** to active CsF resulted in quantitative rearrangement of **6** to **9**. An attempt at formation of the postulated intermediate **10**, by use of the less active RbF, led only to slow formation of **9**.

We believe compound **9** to be the first example of an azopentafluorosulfur species. It is a stable, volatile (extrapolated bp 16 °C), very pale yellow liquid that shows no tendency to degrade under the conditions of its synthesis. The ^{19}F NMR spectrum supports an all-trans structure for **9**: a typical second-order pattern indicative of an SF_5 group is seen, with a slightly broadened (possibly due to the quadrupolar ^{14}N) singlet seen for the CF_3 group. If the configuration of **9** was cis, one might expect a more complex spectrum, due to through-space interaction of the SF_5 and CF_3 groups.

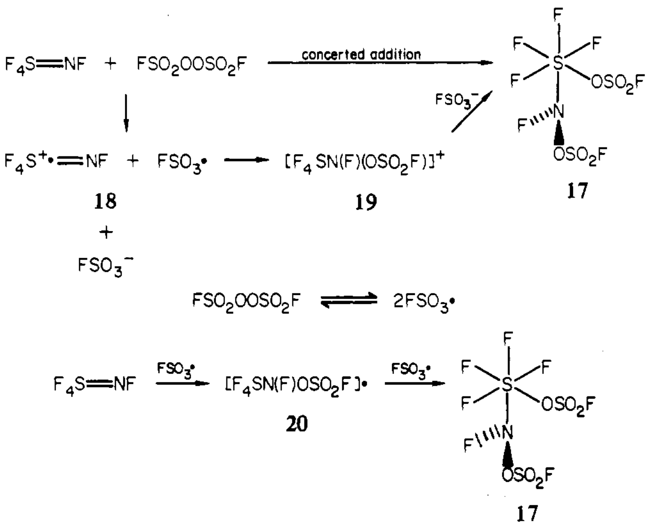
Addition of $XOSO_2F$ (X = Cl, Br, OSO_2F) to $F_4S{=}NF$. (Fluoroimido)tetrafluorosulfur reacted readily with $ClOSO_2F$ and $BrOSO_2F$ at low temperatures, and with FSO_2OOSO_2F at higher temperature, to form the unusual octahedral sulfur compounds *cis*-$SF_4(OSO_2F)NFX$. (One other addition of this type, that of ClF to $(CF_3)F_3S{=}NCF_3$, to give the cis adduct, has been reported by other workers.[6a]) In the cases where $ClOSO_2F$ or $BrOSO_2F$ were used, transient color changes were noted when the reactants were mixed, indicating the possible intermediacy of polar species such as **11** or **12**. The inter-

$$\underset{\mathbf{11}}{XOSO_2F^{+}\cdot SF_4NF^{-}\cdot} \qquad \underset{\mathbf{12}}{F_4S{=}NXF^{+}FSO_3^{-}}$$

$$X = Br, Cl$$

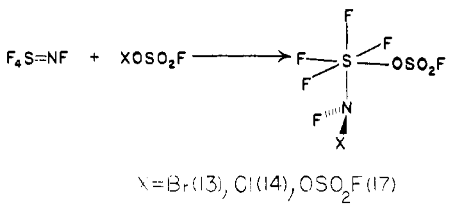
mediate formed in the $ClOSO_2F$ case was very short-lived, being detected only by a brief flash of red color as the reactants mixed at low temperature. In contrast, the dark brown-violet species derived from the initial interaction of $BrOSO_2F$ and

Scheme II



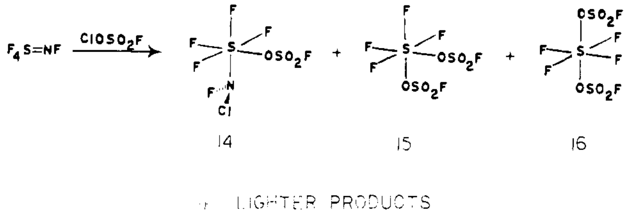
$F_4S{=}NF$ appeared to be stable indefinitely at −45 °C. Further warming caused the color to fade, with concomitant formation of colorless *cis*-$SF_4(OSO_2F)NBrF$ (**13**).

While *cis*-$SF_4(OSO_2F)NBrF$ was the only major heavy product formed in the reaction of $BrOSO_2F$ with $F_4S{=}NF$ (eq 8), an analogous situation was not seen for the reaction



(8)

of $ClOSO_2F$ with $F_4S{=}NF$. In this case, *cis*-$SF_4(OSO_2F)NClF$ (**14**), *cis*-$SF_4(OSO_2F)_2$ (**15**), and *trans*-$SF_4(OSO_2F)_2$ (**16**) were obtained, in a molar ratio of 64:15:21 (eq 9). This



(9)

is apparently the first observation of *trans*-$SF_4(OSO_2F)_2$ (identified by NMR), though the cis isomer has long been known. The reason for the formation of these products in this case may lie in the apparent greater exothermicity of the reaction, compared to that of the $BrOSO_2F$ and FSO_2OOSO_2F reactions. Local heating could cause breakage of the S–N and/or N–Cl bonds of *cis*-$SF_4(OSO_2F)NFCl$, leading eventually to the observed products.

Compound **14** and especially compound **13** were thermally unstable at room temperature, decomposing with release of Cl_2 and Br_2, respectively. Thus, characterizations of **13** and **14**, as well as of *cis*- and *trans*-$SF_4(OSO_2F)_2$ (both admixed with **14**), were done by ^{19}F NMR, as described later.

Peroxydisulfuryl difluoride reacted (eq 8) smoothly with $F_4S{=}NF$, upon gradual warming, to afford *cis*-$SF_4(OSO_2F)N(F)OSO_2F$ (**17**) in 71% yield. Unlike its halogenated analogues, **17** is thermally stable at 23 °C. It is a colorless liquid having an equilibrium vapor pressure of ca. 6 torr at 23 °C. It was characterized primarily by its infrared and ^{19}F NMR spectra. Neither chemical ionization nor electron impact mass spectra showed a molecular ion. This result is not surprising, as we have found this to be a general characteristic of covalent fluorosulfates.

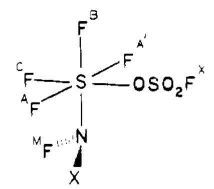


Figure 1. Generalized structure of one enantiomer of the addition products derived from $F_4S{=}NF$ (X = Cl, Br, OSO_2F).

The reaction of $F_4S{=}NF$ with the nonpolar but intensely reactive FSO_2OOSO_2F could proceed by a concerted addition of the peroxide to the double bond of $F_4S{=}NF$, by way of a radical ion or by a stepwise radical addition, as illustrated in Scheme II. The concerted process seems most likely, since the reaction is slower than the analogous reactions involving $BrOSO_2F$ and $ClOSO_2F$ (both polar molecular), and one would expect production of a mixture of *cis*- and *trans*-$SF_4(OSO_2F)N(F)OSO_2F$ if the product were formed by way of cation **19** or radical **20**.

^{19}F NMR Spectra of *cis*-$SF_4(OSO_2F)NFX$ (X = Cl, Br, OSO_2F). The compounds **13**, **14**, and **17** have complex and highly characteristic ^{19}F NMR spectra, which establish the configurations of **13**, **14**, and **17** to be exclusively cis. In addition, the chemical shifts of fluorines A and A′ (Figure 1) were found, for all three compounds, to be different. This difference is attributable to the influence of the neighboring chiral NFX group. Since *N*-fluoroamines are known to have high barriers to inversion, one would expect the NFX group to maintain its configuration, under the conditions of the measurements, thus providing a different magnetic environment for each of the fluorines A and A′.

The spectrum of **14** proved to be the most amenable to interpretation, even though it contained, in addition to the absorptions of **14**, those due to *cis*- (**15**) and *trans*-$SF_4(OSO_2F)_2$ (**16**). Inspection of expanded segments of this spectrum (Figure 2) clearly shows the presence of the three major components (**14**, **15**, and **16**). The absorptions due to *trans*-$SF_4(OSO_2F)_2$ are straightforward: a simple triplet (Figure 2a) due to the SF_4 group and a simple quintet (Figure 2d) due to the two OSO_2F groups, with $^4J_{FF}$ = 7 Hz. The spectrum of *cis*-$SF_4(OSO_2F)_2$ (Figure 2a,b,d) is more complex but is very similar to the 60-MHz spectrum of that compound reported in ref 11n.

Assignments of the resonances of *cis*-$SF_4(OSO_2F)NFCl$ were, despite the complexity of their fine structure, fairly straightforward. The integrated intensities allowed assignment of the central complex multiplets (Figure 2c) to fluorines A and A′, although an actual distinction between the two cannot be made. The fluorosulfate multiplets occurred at values characteristic of that group (Figure 2d). The N–F absorption was distinguished by its broadness (due to quadrupolar effects of ^{14}N). The absorptions due to fluorines B and C were differentiated on the basis of two considerations. First, one would expect the fluorine B, cis to a fluorosulfate and three fluorines octahedrally coordinated to sulfur, to have a chemical shift in the same region as that of the similarly situated fluorines in *cis*-$SF_4(OSO_2F)_2$. This allows tentative assignment of the furthest downfield "quartet" to fluorine B. In addition, it was found that the chemical shifts of certain of the fluorines in this compound were markedly temperature dependent (this effect was even more pronounced for **13** and **17**). The furthest upfield "quartet" is shifted downfield, and the multiplets due to fluorines A and A′ are shifted upfield, when the temperature is lowered. The far-downfield "quartet" is, in each case, only slightly affected. We assume that these effects are linked in some way to rotation of the NFCl group. If this is the case,

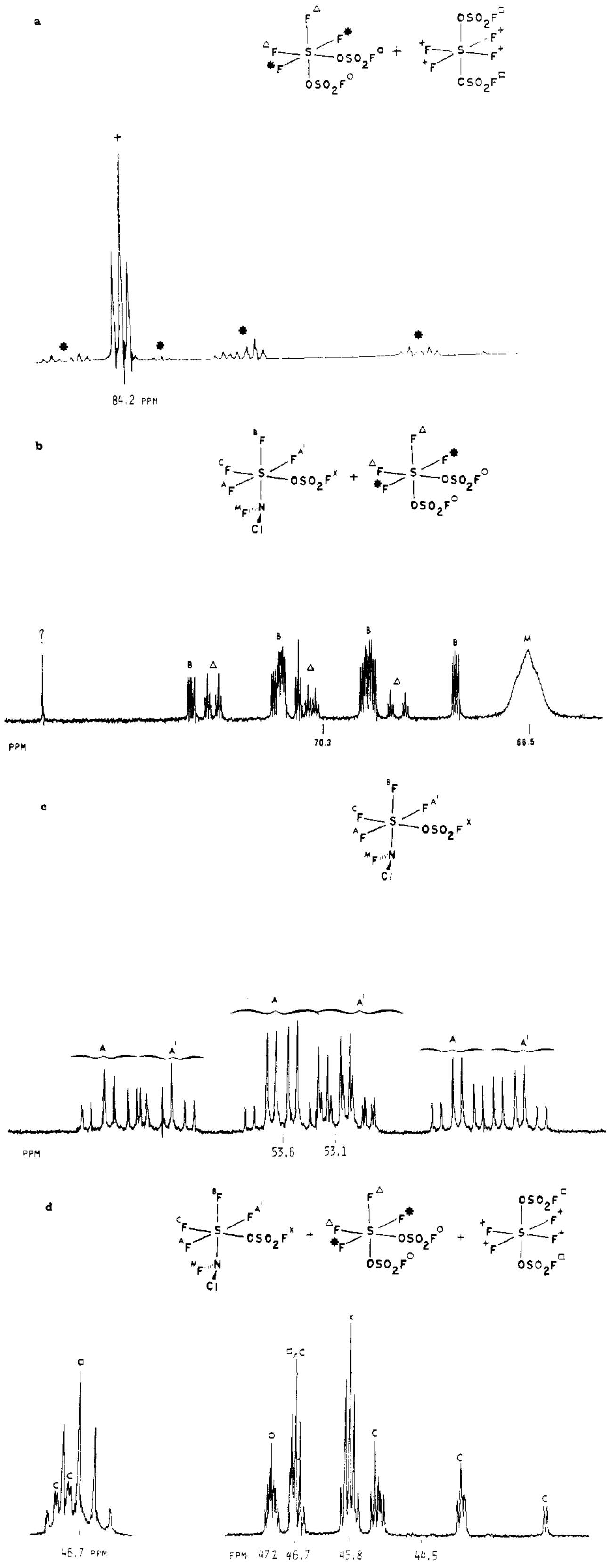


Figure 2. ^{19}F NMR (94.1 MHz) spectrum of a mixture of *cis*-$SF_4(OSO_2F)_2$, *trans*-$SF_4(OSO_2F)_2$, and *cis*-$SF_4(OSO_2F)NFCl$: (a) *cis*-$SF_4(OSO_2F)_2$ and *trans*-$SF_4(OSO_2F)_2$ (+) at −21 °C and 500-Hz sweep width; (b) *cis*-$SF_4(OSO_2F)_2$, F^B of *cis*-$SF_4(OSO_2F)NClF$ (B), and F^M of *cis*-$SF_4(OSO_2F)NClF$ (M) at −70 °C and 1000-Hz sweep width; (c) F^A and $F^{A'}$ of *cis*-$SF_4(OSO_2F)NClF$ (A, A′) at −70 °C and 500-Hz sweep width; (d) *cis*-$SF_4(OSO_2F)_2$, *trans*-$SF_4(OSO_2F)_2$, F^C of *cis*-$SF_4(OSO_2F)NClF$ (C), and F^X of *cis*-$SF_4(OSO_2F)NClF$ (X) at −70 °C and 1000-Hz sweep width (right), with a 250-Hz sweep width expansion of multiplet at δ 46.7 (left).

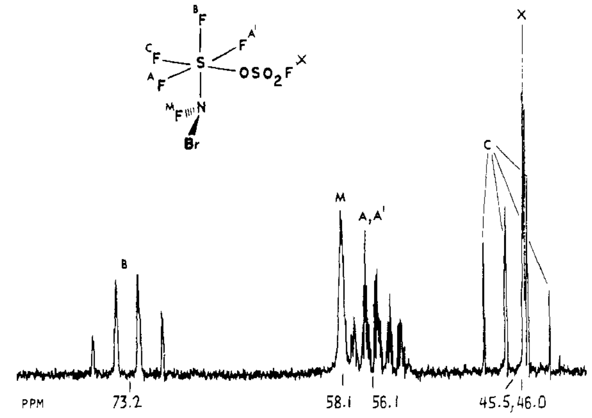


Figure 3. ^{19}F NMR (94.1 MHz) spectrum of *cis*-$SF_4(OSO_2F)NBrF$ at −51 °C and 5000-Hz sweep width.

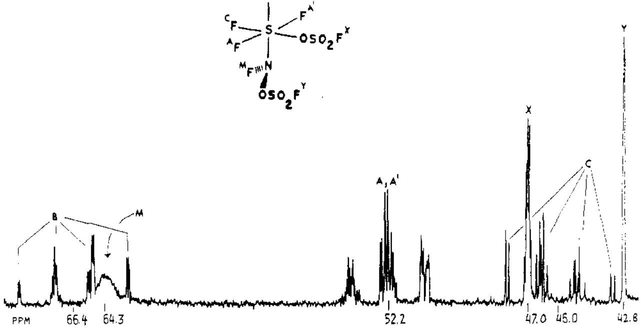


Figure 4. ^{19}F NMR (94.1 MHz) spectrum of *cis*-$SF_4(OSO_2F)NF(OSO_2F)$ at 30 °C and 2500-Hz sweep width.

one would expect the fluorines cis to the NFCl group to be the ones most affected, while the trans fluorine should be the least affected. This consideration allows assignment of the upfield "quartet" to fluorine C and also supports the earlier assignment of the downfield "quartet" to fluorine B.

The spectra of **13** and **17** were interpreted in an analogous manner. The spectra and details of the interpretations are shown in Figures 3 and 4.

Attempts at computer simulation of the NMR spectrum of **14** were only partly successful, with good agreement between all parts of the experimental and simulated spectra not being obtained. The appearance of the simulated spectra did support, however, the assignment of a 7.5-Hz coupling between the trans fluorines A and A′ in compound **14**. Attempts at simulation of the spectra of **13** and **17** were not made, due to the difficulty of assigning the often badly overlapped lines.

Self-Reaction of $F_4S{=}NF$ under F^--Catalytic and Photolytic Conditions. One might suppose that $F_4S{=}NF$ could be induced to form a linear dimer, $SF_5NF(F_3)S{=}NF$, by analogy with the previously mentioned fluoride-induced dimerization of $F_2C{=}NF$ (eq 6 and 7). This expectation, however, was not realized. Instead, $F_4S{=}NF$, when allowed to interact with active KF, was destroyed fairly rapidly, with concomitant formation of N_2, SF_4, and SF_6. In some runs, small quantities of a heavier material were obtained. Analysis of this substance showed it to be not the expected dimer but, rather, the unusual amine $(SF_5)_2NF$ (**21**), one of the few known examples[5] of the small class of geminal bis(pentafluorosulfur) compounds, some others being $(SF_5)_2CF_2$,[11m,21] $(SF_5)_2NSCF_3$,[5] $(SF_5)_2NCl$,[5] $(SF_5)_2N^-$,[5] and $(SF_5)_2O$.[22] The structure of $(SF_5)_2NF$ was confirmed by comparison of its spectral properties with those

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(21) Shimp, L. A.; Lagow, R. J. *Inorg. Chem.* **1977**, *16*, 2974.

(22) (a) Roberts, H. L. *J. Chem. Soc.* **1960**, 2774. (b) Oberhammer, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1435.

recently reported for it by others,[5] who obtained it by the reaction of $Cs^+(SF_5)_2N^-$ with F_2.

The mechanism for the formation of **21** is clearly complex and may well be due to the formation of an intermediate anion, $SF_5NFSF_4NF^-$, in analogy to the formation of $CF_3NFCF_2NF^-$ from $F_2C{=}NF$ and F^-:

$$F_4S{=}NF \xrightarrow{F^-} \mathbf{1} \xrightarrow{F_4S=NF} \mathbf{21} + \text{other products}$$

In contrast to its chlorinated analogue, $F_4S{=}NCl$,[23] which spontaneously dimerizes to a cyclic four-membered ring compound, $(F_4SNCl)_2$,[11q] $F_4S{=}NF$ shows no tendency to form such a dimer, even when heated. In another attempt to induce dimerization, photolysis of $F_4S{=}NF$ was tried. After 1 h of ultraviolet irradiation through Pyrex glass, $F_4S{=}NF$ was recovered unchanged. Irradiation through quartz resulted in partial decomposition of $F_4S{=}NF$, with production of products similar to those found after its decomposition in the presence of KF. These included SF_4, SF_6, N_2, and, interestingly, $(SF_5)_2NF$ (**21**). In this case, the formation of **21** may proceed by a mechanism similar in many respects to that proposed by others[5a,c,d,f] for the formation of $F_4S{=}NSF_5$ from F_2 and NSF_3.

Acknowledgment. Support of this research by the National Science Foundation (Grant Nos. CHE 8116043 and 8217217) and the Army Research Office (Grant Nos. DAAG29-82-K-0188 and DAAG29-80-C-0102) is gratefully acknowledged. D.D.D. acknowledges the Alexander von Humboldt Stiftung for a fellowship during part of this research.

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[23] $SF_4{=}NCl$ has never been isolated, but it is assumed to be the precursor to the cyclic dimer.[11q]

Notes

Contribution from the Department of Chemistry,
University of Connecticut, Storrs, Connecticut 06268

Chemistry of Bipyridyl-like Ligands. 3. Complexes of Ruthenium(II) with 2-((4-Nitrophenyl)azo)pyridine[1]

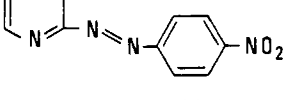
Ronald A. Krause* and Kirsten Krause

Received June 1, 1983

In recent years we have been studying the influence of π-accepting ligands on the properties of transition-metal complexes. As a ligand of this type, 2-(phenylazo)pyridine (Azpy) on ruthenium(II) has proven to be very fruitful in studies both by us[2,3] and others.[4–6] The ligand properties of Azpy have been shown to be related to the strong π-acidity of this compound; a variety of mixed-ligand complexes can be isolated,[3,5,6] and this has led to a useful infrared probe for ruthenium–ligand π-bonding.[3]

Azpy is a stronger π-acid ligand than is 2,2′-bipyridyl (bpy);[3,6] it is now of interest to us to determine the effects of even greater ligand π-accepting properties on ruthenium(II) complexes. The effect of electron-withdrawing substituents on bpy is known to further stabilize ruthenium(II).[7] However, in Azpy the phenyl ring can undergo rotation, affecting conjugation with the azo group, and thus reduce inductive effects on the metal–ligand bond.

In the present work we have attempted to demonstrate the effect of a substituent on the Azpy phenyl ring by preparing ruthenium(II) complexes of 2-((4-nitrophenyl)azo)pyridine (NAz).



NAz

NAz should be a stronger π-acid than Azpy, and this property should be reflected in its complexes. That this is indeed so is shown in the present work.

Table I. Differential Pulse Voltammetry in Acetonitrile Solutions (0.10 M $NaClO_4$) vs. Ag Wire

compd	peak potentials, V
	Anodic Scan
$[Ru(NAz)_2Cl_2]$	(α) 1.27 (137),[a] (β) 1.22 (142), (γ) 1.07 (137)
$[Ru(Azpy)_2Cl_2]$	(α) 1.11 (137), (β) 1.10 (137), (γ) 0.97 (141)
ferrocene	0.383 (135)
	Cathodic Scan
$[Ru(NAz)_3](ClO_4)_2$	0.015 (130), −0.265 (130), −0.608 (142),[b] −0.737, −0.785[c]
$[Ru(Azpy)_3](ClO_4)_2$	−0.116 (126), −0.433 (126), −0.913 (134)

[a] Peak width (mV) at half-height given in parentheses. [b] Peak not completely separated from the following one; estimated by assuming symmetrical shape. [c] Two peaks, slightly separated; half-width 134 mV.

Experimental Section

Materials. Reagents were used as received. $RuCl_3 \cdot 3H_2O$ was purchased from Matthey Bishop, Inc., Malvern, PA; organic chemicals were from Aldrich Chemical. 2-(4-Nitrophenyl)azo)pyridine was prepared as reported by Pentimalli.[8] Thin-layer-chromatography (TLC) plates were precoated TLC sheets, Silica Gel 60F-254, from EM Laboratories, Inc., Elmsford, NY.

Methods. Physical measurements were performed as previously described.[2,3] Differential-pulse voltammetry was performed with a PAR electrochemical unit, Model 170, using a three-electrode system (platinum microdisk working electrode, platinum wire counterelectrode, and silver wire reference electrodes). Spectrograde acetonitrile, 0.10 M in sodium perchlorate, was used as the solvent; solutions were degassed with nitrogen. The scan rate was 2 mV/s, and pulse height was 10 mV.

Observed peak emf values are reported in Table I. For comparison with other systems both cyclic voltammetry and differential-pulse voltammetry were performed on ferrocene under identical conditions. CV on ferrocene gave a formal potential (vs. Ag wire) of 0.324 V. Using the value of 0.400 V (NHE)[9] establishes the potential of the reference at 0.076 V.

Analyses were performed by Baron Consulting Co., Orange, CT; prior to analysis samples were redried in vacuo at 110 °C.

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[1] Presented at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; see Abstracts, No. INOR 172.
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