

ports the assigned structure. The spectrum consists of a septuplet ($J_{\text{FF}} = 8$ c.p.s.) at $\phi - 57.2$, which is assigned to the fluorines bound to sulfur, and a triplet ($J_{\text{FF}} = 8$ c.p.s.) at $\phi 48.2$, which is assigned to the fluorine atoms on carbon. The respective relative area ratio is 1.0:3.1. Thus the two perfluoromethyl groups must be equivalent. The spectrum of $(\text{C}_2\text{F}_5\text{N}=\text{S})_2\text{SF}_2$ is similar and consists of a quintuplet ($J_{\text{FF}} = 8$ c.p.s.) centered at $\phi - 63.1$, which is assigned to the SF_2 group. The quintuplet arises from coupling with two equivalent CF_2 groups. The bands in the C—F region consist of a triplet ($J_{\text{FF}} = 8$ c.p.s.) centered at $\phi 86.5$ which overlaps with a singlet at slightly lower field. The triplet is assigned to the CF_2 group and the singlet to the CF_3 group. Apparently the CF_2 group and the CF_3 group do not couple. The area ratio due to the SF_2 , CF_3 , and CF_2 group fluorine atom resonances is 2.0:5.9:4.1, respectively. The ^{19}F n.m.r. spectra of the saturated products, CF_3NFSF_3 and $\text{C}_2\text{F}_5\text{NFSF}_3$, are more complex. No attempt was made to analyze the bands attributable to the SF_3 groups which have AB_4 patterns. The major bands of these groups are centered at $\phi - 58.2$ and -60.5 for CF_3NFSF_3 and $\text{C}_2\text{F}_5\text{NFSF}_3$, respectively. The two other bands in the spectrum of CF_3NFSF_3 are found at $\phi 48.2$ and 70.3 and are assigned to the NF and CF_3 groups. The area ratio for $\text{SF}_3:\text{NF}:\text{CF}_3$, 5.1:1.0:3.1, respectively, is consistent with the assignments. In the spectrum of $\text{C}_2\text{F}_5\text{NFSF}_3$ the broad band at $\phi 49.4$ is assigned to the NF fluorine while the doublet ($J_{\text{FF}} = 10$ c.p.s.) at $\phi 81.7$ and the band at $\phi 110.1$ are assigned to the CF_3 and CF_2 groups, respectively. The band at $\phi 81.7$ coalesced into a singlet when the band at $\phi 49.4$ was saturated. Therefore the fluorines on the CF_3 and NF groups are coupled while the fluorines on the CF_2 group do not couple with those on the CF_3 group. The ratio of the areas of the SF_3 , NF , CF_3 , and CF_2 group

fluorine resonances is 4.63:1.0:3.17:1.90, respectively, and is, again, consistent with the above assignment.

The observation that the CF_3 groups and the C_2F_5 groups in $(\text{CF}_3\text{N}=\text{S})_2\text{SF}_2$ and $(\text{C}_2\text{F}_5\text{N}=\text{S})_2\text{SF}_2$, respectively, are equivalent and the evidence from the infrared and mass spectra for the presence of an $\text{S}=\text{N}$ bond in these compounds support the above proposed formulation. An alternate possibility which must be considered is $\text{R}_2\text{NN}=\text{SF}_2$. Some evidence against this formulation is found in the mass spectrum of $(\text{C}_2\text{F}_5\text{N}=\text{S})_2\text{SF}_2$. Peaks corresponding to ions which contain one carbon, one nitrogen, and one sulfur are found (*e.g.*, 115, CNSF_3^+ , 2.7%; 134, CNSF_4^+ , 17.0%; and 153, CNSF_5^+ , 13.5%). These fragments cannot arise from the above structure unless a rearrangement involving the formation of a C—N bond occurred. This is felt to be unlikely. Similar peaks are observed in the mass spectrum of $(\text{CF}_3\text{N}=\text{S})_2\text{SF}_2$. Furthermore, $(\text{CF}_3\text{N}=\text{S})_2\text{SF}_2$ is resistant to hydrolysis, being unaffected by aqueous 20% solutions of sodium hydroxide or hydrochloric acid at reflux for 4 hr. This is analogous to the behavior of SO_2F_2 . The N—N structure presumably would not resist hydrolysis to this extent.

Attaway and co-workers⁷ reported an unstable compound having the tentatively assigned structure $\text{SF}_3\text{CF}_2\text{NF}_2$, but Roberts speculates that an alternate structure, SF_5NFCF_3 ,⁸ is more likely. Nevertheless, no structural characterization has been given prior to that reported in this paper which is consistent with the monofluoramine structure.

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The Imidodisulfuryl Fluoride Ion

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Imidodisulfuryl fluoride is an acid in aqueous media, and several salts containing the $\text{N}(\text{SO}_2)\text{F}_2$ anion have been prepared. The silver salt forms a stable complex with benzene. Cesium imidodisulfuryl fluoride behaves as a 1:1 electrolyte in nitromethane.

Although the chemistry of imidodisulfuryl fluoride has not been extensively investigated,^{1,2} the reported observations indicate that the nitrogen possesses little

basicity.¹ In fact, imidodisulfuryl fluoride exhibits acidic behavior toward ammonia. It was suggested that ammonium imidodisulfuryl fluoride was formed, but no conclusive evidence was presented.¹ This investigation was undertaken in order to characterize further the imidodisulfuryl fluoride ion.

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TABLE I
 SUMMARY OF THE IMIDO DISULFURYL FLUORIDE DERIVATIVES

Compound	M.p. [b.p. (mm.)]	Yield, ^a %	Metal, %		N, %		F, %		C, %		H, %		Purification
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
AgN(SO ₂ F) ₂	147–149°	95	37.9	37.5	4.64	4.86	12.7	13.2					Extrn. with water
AgN(SO ₂ F) ₂ ·C ₆ H ₆	121–123°	91	29.6	29.5	3.83	3.83	10.0	10.4	19.49	19.69	1.65	1.64	R ₂ CH ₂ Cl ₂
KN(SO ₂ F) ₂	100–101°	45	17.5	17.8	6.41	6.39	17.0	17.4					R ₂ C ₂ H ₅ OH
RbN(SO ₂ F) ₂	195–96°	78	32.4	32.3	5.29	5.27	13.8	14.3					R ₂ C ₂ H ₅ OH
CsN(SO ₂ F) ₂	115–117°	85	42.3	42.5	4.48	4.47	12.0	12.1					R ₂ C ₂ H ₅ OH
(CH ₃) ₄ NN(SO ₂ F) ₂	286–288°	80			10.80	11.02			18.95	18.90	4.92	4.72	R ₂ H ₂ O
(C ₆ H ₅) ₃ PCH ₃ N(SO ₂ F) ₂	96–97°	62			2.99	3.15			48.40	48.58	4.00	4.04	R ₂ C ₂ H ₅ OH– (C ₂ H ₆) ₂ O
CH ₃ N(SO ₂ F) ₂	[70° (57)]	71			7.24	7.18	19.1	19.5	6.61	6.15	1.62	1.59	Distillation
C ₂ H ₅ N(SO ₂ F) ₂	[75° (61)]	65			6.89	6.70	17.9	18.2	11.65	11.48	2.57	2.39	Distillation

^a Yield based on recrystallized product.

 TABLE II
 INFRARED SPECTRA OF THE IMIDODISULFURYL FLUORIDE SALTS (CM.⁻¹)

HN(SO ₂ F) ₂ ^a
3311 m, 1471 vs, 1337 w, 1248 w, 1217 vs, 923 s, br, 893 m, br, 832 s, br
KN(SO ₂ F) ₂ ^b
1402 m, 1377 vs, 1224 s, 1185 vs, 1127 m, 1115 m, 861 vs, 847 vs, 785 s, 749 s, 729 s
RbN(SO ₂ F) ₂ ^b
1935 vw, 1839 vw, 1379 vs, 1224 w, 1176 vs, 1094 s, 894 s, 826 sh, 769 vs, 738 s
CsN(SO ₂ F) ₂ ^b
1940 vw, 1836 vw, 1379 vs, 1222 w, 1179 vs, 1101 s, 843 s, 820 sh, 763 vs, 729 vs
HgN(SO ₂ F) ₂ ^b
1923 vw, 1842 vw, 1389 vs, 1200 w, 1174 vs, 1062 vw, 906 s, 851 s, 800 vs
(CH ₃) ₄ NN(SO ₂ F) ₂ ^b
1923 vw, 1842 vw, 1490 m, 1388 vs, 1220 m, 1181 vs, 1094 s, 951 s, 835 vs, 813 w, sh, 746 vs, br
N(SO ₂ F) ₂ ^c
1406 m, 1221 w, 1190 vs, 1110 s, 835 s, 750 vs, br, 734 sh

^a Captive layer on AgCl plates. ^b Taken as Nujol smears. Nujol bands omitted. ^c KN(SO₂F)₂ in CH₃CN solution.

Experimental

A summary of the compounds prepared and the analytical data is presented in Table I.

Preparation of the Alkali Metal Salts.—The potassium, rubidium, and cesium salts were prepared in an analogous manner. A typical procedure is: 16.72 g. (0.0924 mole) of HN(SO₂F)₂, prepared by the literature method,^{1,2} was placed in a round-bottom flask and cooled to –78°. Then 50 ml. of water was added. After the solution had warmed to 25°, 6.31 g. (0.0457 mole) of potassium carbonate was slowly added. The water was removed under vacuum and the solid residue was recrystallized from ethanol.

Preparation of AgN(SO₂F)₂ and AgN(SO₂F)₂·C₆H₆.—A solution containing 19.8 g. (0.109 mole) of HN(SO₂F)₂ in 40 ml. of trifluoroacetic acid was placed in a round-bottom flask. Silver oxide, 11.6 g. (0.050 mole), was added to the solution by means of a solid addition funnel. The mixture was warmed to 50° and stirred for 1 hr. It was then filtered and the solid washed with methylene chloride.

If AgN(SO₂F)₂·C₆H₆ is desired the above procedure may be carried out using benzene instead of CF₃COOH. After the addition of silver oxide, the mixture is stirred for 10 min. and then dried by the addition of magnesium sulfate. The mixture was filtered and the benzene removed from the filtrate under vacuum. The solid residue was recrystallized from methylene chloride.

Preparation of CH₃N(SO₂F)₂ and C₂H₅N(SO₂F)₂.—To a solution of 15.2 g. (0.0415 mole) of AgN(SO₂F)₂·C₆H₆ in 100 ml. of CH₂Cl₂, methyl iodide, 8.82 g. (0.0621 mole), was added. The mixture was stirred 2 hr. and then filtered. The solvent was removed from the filtrate by distillation. The residue was then distilled through a Holtzmann column. The ethyl derivative was prepared in an analogous manner.

Reaction of (CH₃)₃N and CH₃N(SO₂F)₂.—A 1.75-g. (8.53 mmoles) sample of CH₃N(SO₂F)₂ was put in a 35-ml. pressure reactor equipped with a Teflon needle valve. Methylene chloride, 5 ml., was added and then trimethylamine, 0.596 g. (10.1 mmoles), was condensed into the reactor. The mixture was stirred for 18 hr. All of the volatile components of the mixture were removed under vacuum at 25°. The solid residue was recrystallized from water and 1.79 g. (82% yield) of product was obtained. When the above reaction was repeated using triphenylphosphine instead of trimethylamine, the salt (C₆H₅)₃PCH₃N(SO₂F)₂ was isolated.

Analyses.—Nitrogen analyses were by the Dumas method. Fluorine analyses were performed by hydrolyzing the sample with 30% aqueous KOH at 100° for several days and determining the fluoride content of the solution by the thorium nitrate method. The alkali metals were determined gravimetrically as their tetraphenylborates. They could also be determined as their sulfates by the sulfate ash method.

Infrared Spectra.—The infrared spectra of the salts taken with a Perkin-Elmer Model 21 spectrometer are tabulated in Table II. The infrared spectrum of HN(SO₂F)₂ is also included. It was found that some of the bands previously reported for HN(SO₂F)₂² were due to impurities formed by reaction of HN(SO₂F)₂ with the sodium chloride plates. Therefore, silver chloride plates, which proved inert to HN(SO₂F)₂, were used.

Mass Spectrum of CH₃N(SO₂F)₂.—A 5-μl. sample of CH₃N(SO₂F)₂ was injected into the inlet system of a Consolidated Engineering Corp. Model 21-620 spectrometer. The mass number, species, and relative abundance for some of the more prominent peaks are as follows: 28, CH₂N⁺, 100%; 67, SOF⁺, 30.4%; 83, SO₂F⁺, 26.2%; 112, CH₃NSO₂F⁺, 19.8%; 84, HSO₂F⁺, 19.2%; 29, CH₃N⁺, 14.4%; 92, CH₂NSO₂⁺, 14.1%;

194, $\text{CH}_2\text{N}(\text{SO}_2\text{F})_2^+$, 10.8%; 48, SO^+ , 7.3%; 195, $\text{CH}_3\text{N}(\text{SO}_2\text{F})_2^+$, 7.0%; 15, CH_3^+ (NH^+), 5.8%; 65, SOF^+ , 5.4%; 111, $\text{CH}_2\text{NSO}_2\text{F}^+$, 5.0%.

Ultraviolet Spectrum of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$.—The ultraviolet spectrum of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ was obtained with a Beckman Model DK 1 spectrophotometer on a $4.91 \times 10^{-4} M$ solution in CH_2Cl_2 . A benzenoid type of spectrum was observed. The maxima and extinction coefficients are: λ_{max} 261 $\text{m}\mu$ (ϵ 575), λ_{max} 255 $\text{m}\mu$ (ϵ 780), λ_{max} 249 $\text{m}\mu$ (ϵ 755), λ_{max} 243 $\text{m}\mu$ (ϵ 785), and λ_{max} 229 $\text{m}\mu$ (ϵ 1540) (units of ϵ are l./mole cm^{-1}).

N.m.r. Spectra.—The H^1 n.m.r. measurements were taken with a Varian A-60 spectrometer and the F^{19} n.m.r. measurements with a Varian Model V4310A spectrometer operating at 40 Mc. Tetramethylsilane and CCl_3F were used as standards. The H^1 n.m.r. spectrum of neat $\text{HN}(\text{SO}_2\text{F})_2$ consisted of a single band at -8.60 p.p.m. and the F^{19} n.m.r. spectrum was a single band at $\phi - 58.5$. The latter band was shifted to $\phi - 52.4$ in water. The position of the single band in the F^{19} n.m.r. spectra of the salts either in water or in CH_3CN was also at $\phi - 52.4 \pm 0.2$. The H^1 and F^{19} n.m.r. spectra of $\text{CH}_3\text{N}(\text{SO}_2\text{F})_2$ and $\text{C}_2\text{H}_5\text{N}(\text{SO}_2\text{F})_2$ were taken in 5% CCl_4 solutions. The results are: $\text{CH}_3\text{N}(\text{SO}_2\text{F})_2$, H^1 , triplet -3.64 p.p.m. ($J_{\text{HF}} \approx 2$ c.p.s.), F^{19} , singlet $\phi - 59.1$; $\text{CH}_3\text{CH}_2\text{N}(\text{SO}_2\text{F})_2$, H^1 (CH_3), triplet -1.53 p.p.m. ($J_{\text{HH}} = 7$ c.p.s.), H^1 (CH_2), two quadruplets ($J_{\text{HH}} = 7$ c.p.s., $J_{\text{HF}} \approx 2$ c.p.s.), F^{19} , singlet, $\phi - 58.6$. The H^1 and F^{19} n.m.r. spectra of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$, taken in 5% CH_2Cl_2 solution, occurred as single bands at -7.60 p.p.m. and $\phi - 52.6$, respectively.

Molecular Weight Data.—Cryoscopic molecular weights were obtained in an apparatus previously described.³ The freezing point depressions of solutions containing 1.6491 g. of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ and 25.9256 g. of benzene, 3.0751 g. of salt and 23.5874 g. of benzene, and 5.9646 g. of salt and 23.5874 g. of benzene were 0.41, 0.55, and 0.81°, respectively. The average molecular weights found for three runs on each of the above solutions were 800 ± 10 , 1080 ± 20 , and 1480 ± 25 , respectively. The ebullioscopic molecular weight determination was done in a Cottrell apparatus using triphenylmethane as a standard. The average molecular weight of 0.6072 g. of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ in 26.0520 g. of methylene chloride found for two runs was 600 ± 20 .

pH Measurements.—The pH titration at $25 \pm 0.5^\circ$ of 0.1960 g. of $\text{HN}(\text{SO}_2\text{F})_2$ in 25 ml. of water with 0.1107 *N* NaOH solution was followed with a Beckman Model G pH meter. The end point occurred after the addition of 9.89 ml. of NaOH solution. The $\text{p}K_a$ of $\text{HN}(\text{SO}_2\text{F})_2$ was calculated at 25, 50, and 75% neutralization and gave a value of 1.28 ± 0.02 . Another titration gave a value of the $\text{p}K_a$ of 1.29 ± 0.02 .

Conductance Measurements.—The conductance measurements were performed at $25 \pm 0.2^\circ$ using the equipment previously described.⁴ Spectral grade nitromethane which had been dried over Linde 5A Molecular Sieves and had a specific conductivity of 3.5×10^{-7} ohm $^{-1}$ was used as solvent. The cell employed had a cell constant of 0.1674 cm^{-1} . The concentration (*M*) and the observed equivalent conductance ($\text{cm}^2/\text{ohm equiv.}$) are: 1.319×10^{-2} , 89.7; 7.176×10^{-3} , 96.4; 6.595×10^{-3} , 97.3; 3.588×10^{-3} , 101.6; 3.298×10^{-3} , 102.8; 1.794×10^{-3} , 106.0; 1.649×10^{-3} , 106.6; 8.254×10^{-4} , 108.9; and 4.123×10^{-4} , 111.5. This gives a value of the equivalent conductance at infinite dilution of 115.5 $\text{cm}^2/\text{ohm equiv.}$

Results and Discussion

Imidodisulfuryl fluoride dissolves in water to produce an acidic solution. Titration of this solution with aqueous sodium hydroxide results in a titration curve typical of a strong acid, and an equivalent weight of 179 (calcd. 181) was found for imidodisulfuryl fluoride. The value of 1.28 ± 0.02 for the $\text{p}K_a$ of imidodisulfuryl fluoride indicates that it is about as strong an acid as periodic acid and is slightly stronger than oxalic acid.

Neutralization of aqueous imidodisulfuryl fluoride with either potassium, rubidium, or cesium carbonate led to the isolation of the corresponding imidodisulfuryl fluoride salts. These salts are not hygroscopic and are fairly soluble in polar organic solvents such as acetonitrile, dimethyl sulfoxide, and nitromethane. Their solubility decreases in going from potassium to cesium. Cesium imidodisulfuryl fluoride behaves as a strong electrolyte in nitromethane since the slope of the straight line obtained by plotting $\Lambda_0 - \Lambda$ vs. \sqrt{c} is 224.⁵ These salts are unusual in that they have very low melting points (see Table I).

The silver salt of imidodisulfuryl fluoride can be prepared by reaction of silver oxide with $\text{HN}(\text{SO}_2\text{F})_2$ in trifluoroacetic acid in a manner analogous to that reported for the preparation of silver salts of organic amides.⁶ When this reaction was attempted using $\text{H}_2\text{NSO}_2\text{F}$ instead of $\text{HN}(\text{SO}_2\text{F})_2$ none of the desired salt, AgNHSO_2F , was formed; instead silver trifluoroacetate was obtained. This is probably due to the difference in the acidity of the two sulfuryl derivatives, although the effect of solubility of the two salts on the equilibria involved is unknown. Attempted recrystallization of silver imidodisulfuryl fluoride from various solvents was not successful. However, for use as an intermediate the purity of the crude product was sufficient. Tetramethylammonium imidodisulfuryl fluoride and triphenylmethylphosphonium imidodisulfuryl fluoride are obtained from their chlorides by treatment with aqueous silver imidodisulfuryl fluoride. Both salts are nonhygroscopic and tetramethylammonium imidodisulfuryl fluoride can be recrystallized from boiling water without decomposition. The tetramethylammonium salt was also much higher melting than the alkali metal salts and apparently much less soluble in such solvents as water, ethanol, and acetonitrile. In addition to observing its melting point on a differential thermogram another endotherm was found at 77° . This is probably due to a crystal lattice transition.

Silver imidodisulfuryl fluoride is very soluble in benzene and the complex $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ may be isolated from solution as white, slightly hygroscopic crystals. It is soluble in several slightly polar organic solvents such as diethyl ether and methylene chloride. A more convenient preparation of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ is to use benzene as the solvent in the reaction between silver oxide and $\text{HN}(\text{SO}_2\text{F})_2$. The complex melts at 122° with decomposition, and at 150° , under vacuum, all of the benzene may be removed. The residue is silver imidodisulfuryl fluoride. The structure of the complex in the solid state is probably related to that of $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$.⁷ A cryoscopic molecular weight determination of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ in benzene showed that complete breakdown of the assumed layered structure (observed in the solid state for $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$) did not occur. The observed molecular weight was

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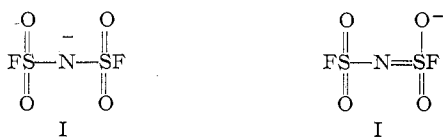
(7) R. E. Rundle and J. H. Goring, *ibid.*, **72**, 5337 (1950).

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(4) J. K. Ruff, *Inorg. Chem.*, **2**, 813 (1963).

found to be a function of concentration and varied between 800 for a 0.17 *m* solution to 1480 for a 0.69 *m* solution. In a 0.064 *m* solution in methylene chloride the molecular weight of the complex was only 600. The proton n.m.r. of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ consists of a single band at -7.60 p.p.m., while the peak due to uncomplexed benzene is observed at -7.38 p.p.m. in the same media. The ultraviolet spectrum of the complex showed an increase in the extinction coefficients for the higher energy benzenoid bands over that observed in benzene.⁸

The greatly reduced electron density on the nitrogen in imidodisulfuryl fluoride ion is a result of the inductive effect of the SO_2F groups and of contributions to the structure of the anion of such resonance forms as II below. The existence of sulfur–nitrogen π bonding

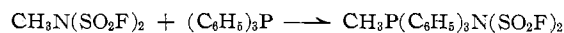
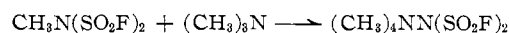


as required by form II has been considered recently by Cruickshank,⁹ who concludes that it occurs to an appreciable extent in sulfamates and other relative derivatives, and X-ray data on the imidodisulfonate ion,¹⁰ $\text{HN}(\text{SO}_3)_2^{-2}$, indicate that appreciable π bonding occurs in this species. The existence of sulfur–nitrogen π bonding in the imidodisulfuryl ion can be inferred from a comparison of the group electronegativities of the SO_2F and $\text{N}(\text{SO}_2\text{F})_2$ groups. Although the determination of group electronegativities from n.m.r. chemical shifts is not strictly rigorous, the method of Cavanaugh and Bailey¹¹ was used to obtain values for these two groups for comparison. The larger group electronegativity of the $\text{N}(\text{SO}_2\text{F})_2$ group (3.6) over that of either nitrogen or the SO_2F group (3.1)¹² is probably a result of delocalization of electrons through sulfur–nitrogen π bonding.

This can also be inferred from infrared spectral data. Resonance structure I of the anion is isoelectronic with pyrosulfuryl fluoride and would thus be expected to have a similar infrared spectrum. In fact, the halo derivatives of imidodisulfuryl fluoride, $\text{XN}(\text{SO}_2\text{F})_2$ (where $\text{X} = \text{F}^2$ or Cl^{13}), in which the halogen is believed to be bonded to nitrogen,² have infrared spectra very

similar to pyrosulfuryl fluoride.¹⁴ The infrared spectrum of the $\text{N}(\text{SO}_2\text{F})_2$ anion, however, is much more complex (see Table II) and contains several additional bands. This increased complexity is believed to reflect sulfur–nitrogen bond orders greater than one. Stabilization of the anion by contributions to the structure of such forms as II would make oxidation difficult. This was found to be the case since attempts to oxidize the $\text{N}(\text{SO}_2\text{F})_2$ ion at a platinum electrode in acetonitrile solutions of tetra-*n*-butylammonium perchlorate were unsuccessful. Perchlorate anion oxidation occurred more easily.

The reaction of methyl or ethyl iodide with $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ produced only one of the two possible alkylated isomers which could be derived from either structure I or II. An unambiguous structural assignment of the products could not be made, but the available evidence suggested that only the N-alkylated isomers were formed. This assignment is based on the mass spectrum of $\text{CH}_3\text{N}(\text{SO}_2\text{F})_2$, which contains a very strong peak corresponding to a molecular ion having a mass of 28 and a peak of medium intensity corresponding to an ion of mass 29. The former peak is not attributable to molecular nitrogen or to carbon monoxide because of the absence of peaks for the N^+ and C^+ ions. These peaks are believed to be due to the ions CH_2N^+ and CH_3N^+ rather than CO^+ and HCO^+ , since no peaks corresponding to the ions CH_2O^+ and CH_3O^+ were found. The H^1 n.m.r. spectrum of $\text{CH}_3\text{N}(\text{SO}_2\text{F})_2$ showed only one type of methyl group which is split into a triplet by coupling with two equivalent fluorines and the F^{19} n.m.r. showed only one type of fluorine. This also supports the above assignment since in the O-alkylated isomer the fluorines would not be equivalent. Methyl imidodisulfuryl fluoride behaves as an alkylating reagent toward amines and phosphines.



This behavior is in contrast to the behavior of typical organic amides and demonstrates one of the unusual properties of the $\text{N}(\text{SO}_2\text{F})_2$ group.

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