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Chemistry of Trifluoromethylsulfinyl Fluoride. Trifluoromethylsulfinamides and Trifluoromethylsulfinate Esters

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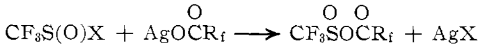
Trifluoromethylsulfinate esters and trifluoromethylsulfinamides result when trifluoromethylsulfinyl fluoride reacts with alcohols and amines. Mercaptans with $CF_3S(O)F$ do not yield the expected thiosulfinates but rather mixed disulfides. The methylene protons of $CF_3CH_2OS(O)CF_3$ and $CH_3CH_2OS(O)CF_3$ are magnetically nonequivalent giving rise to ABM_3X_3 nmr spectra. The new compounds $CF_3S(O)OCH_3$, $CF_3S(O)OCH_2CH_3$, $CF_3S(O)OCH_2CF_3$, $CF_3S(O)N(CH_2CH_3)_2$, $CF_3S(O)N(CH_3)_2$, $(CF_3S(O))_2NCH_3$, and $CF_3S(O)NH_2$ are slightly volatile, colorless liquids.

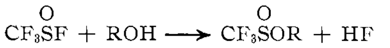
Recently there has been considerable interest in fluorinated >S=O-containing molecules which are obtained primarily *via* the reactions of metal fluorides with dialkyl sulfites[1] or potassium fluorosulfinate[2] with alkyl esters of chlorosulfinic acids. While this work was in progress, Sharp, *et al.*,[3] reported syntheses of several new FS(O)- compounds which permit a comparison of the properties with the analogous $CF_3S(O)$- materials. Little is known about the properties of $CF_3S(O)$- compounds although $CF_3S(O)X$, where X = F, Cl, or Br,[4,5] has been characterized previously.

Trifluoromethylsulfinyl halides react with silver perfluorocarboxylates to form sulfinyl carboxylic anhydrides of moderate stability.[6]



$$CF_3S(O)X + AgO\overset{O}{C}R_f \longrightarrow CF_3\overset{O}{S}O\overset{O}{C}R_f + AgX$$

Partially fluorinated sulfinyl esters have now been prepared by the alcoholysis of trifluoromethylsulfinyl fluoride



$$CF_3\overset{O}{S}F + ROH \longrightarrow CF_3\overset{O}{S}OR + HF$$

where R = CH_3, CH_2CH_3, or CH_2CF_3. The ^1H nmr spectra of the latter two are rather complex ABM_3X_3 systems due to the magnetic nonequivalency of the methylene protons. Analogous reactions with mercaptans, ethanethiol and methanethiol, do not give the thiolsulfinates but rather disulfides

$$CF_3\overset{O}{S}F + RSH \longrightarrow RSSR + RSSCF_3 + H_2O$$

where R = CH_3 or CH_2CH_3. The mercurial $Hg(SCF_3)_2$ reacts with $CF_3S(O)Cl$ to give CF_3SSCF_3 and $CF_3SO_2SCF_3$, but $CF_3S(O)SCF_3$ cannot be isolated.

Sulfenamides (CF_3SNH_2) result from the reaction of CF_3SCl or CF_3SSCF_3 with ammonia or amines.[7-9] Although arenesulfinamides ($RS(O)NR_2$) have been known for many years,[10] amides derived from alkanesulfinic acids were synthesized only after the alkanesulfinyl chlorides were prepared.[11-13] Primary and secondary amines also react with $CF_3S(O)F$ with ease to give mono- and bis(trifluoromethylsulfin)amides, but ammonia appears to give only the monosubstituted product. All of the new compounds reported are colorless liquids of low volatility which are prepared in essentially quantitative yields.

Results and Discussion

Reactions of trifluoromethylsulfinyl fluoride with alcohols provide a direct route to sulfinate esters in high yield. The progress of reaction is easily monitored by the disappearance of the S-F stretching frequency of the $CF_3S(O)F$ in the infrared spectrum of a reaction mixture. While the reaction progresses, the intensity of the SiF_4 band steadily grows as the HF produced in the reaction attacks the glass reaction vessel. Mass spectra of the sulfinate esters show the presence of ions assigned to $ROS(O)^+$ ($M - CF_3$) which range in intensity from 75 to 100% of the base peak.

Fluorine nmr spectra are appropriate multiplets as required (Table I) for simple first-order interactions. It is interesting to note that although coupling of fluorine with only the methylene protons (~0.8 cps) occurs in the ethylsulfinate, in the 2,2,2-trifluoromethylsulfinate ($CF_3CH_2OS(O)CF_3$) the $CF_3S(O)$ fluorines couple with both the methylene protons (~0.75 cps) and the fluorinated methyl group (0.7 cps).

In the proton nmr spectra of $CH_3CH_2OS(O)CF_3$ and $CF_3CH_2OS(O)CF_3$ which are ABM_3X_3 systems (Figures 1 and 2), the methylene protons are observed as multiplets centered at δ 4.26 and 4.45, respectively. The spectra can easily be rationalized based on the magnetic nonequivalency of the methylene protons as has been observed for other fluorosulfinate esters.[1,2] The alkyl fluorosulfites included in Table I for comparison also exhibit magnetic nonequivalence due to the asymmetric center at the sulfur atom. Spectra of $CF_3S(O)OCH_2R$

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TABLE I

^1H AND ^{19}F NMR SPECTRA (PPM)[a]

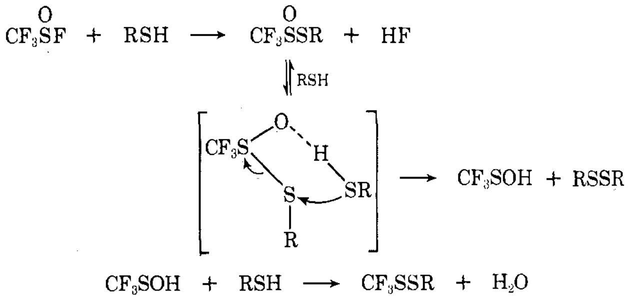
Compd	CH_3	CH_2	βCF_3	CF_3	F	NH_2	J, cps	
$CH_3O\overset{O}{S}F$[1,2]	3.83 (d)				−54.7 (q)		J_{H-F} = 1.2	
$CH_3O\overset{O}{S}CF_3$	3.84 (q)			79.1 (q)			J_{H-F} = 1.2	
$C_2H_5O\overset{O}{S}F$[1,2]	1.35 (t)	4.40 (q of q)			−58.6 (t)		J_{A-M_3} = 7.4 J_{B-M_3} = 7.0 J_{A-B} = 9.8	J_{A-X} = 1.0 J_{B-X} = 1.5
$C_2H_5O\overset{O}{S}CF_3$	1.38 (t)	4.26 (mult)		79.95 (t)			J_{A-B} = 10.0 J_{A-M_3} = 7.3 J_{B-M_3} = 7.1	J_{A-X_3} = 0.6 J_{B-X_3} = 1.1
$CF_3CH_2O\overset{O}{S}CF_3$		4.45 (mult)	79.6 (sext)	75.19 (t of q)			J_{A-B} = 12.6 J_{A-M_3} = 7.9 J_{B-M_3} = 7.6	J_{A-X_3} = 0.6 J_{B-X_3} = 1.0 $J_{M_3-X_3}$ = 0.7
$(C_2H_5)_2N\overset{O}{S}CF_3$	1.18 (t)	3.32 (q of q)		77.3 (pent)			$J_{A_2-M_3}$ = 7.2 $J_{A_2-X_3}$ = 0.8	
$(CH_3)_2N\overset{O}{S}CF_3$	2.84 (q)			75.4 (sept)			J_{H-F} = 1.4	
$CH_3N(\overset{O}{S}CF_3)_2$	2.76 (sept)			74.6 (q)			J_{H-F} = 1.5	
$H_2N\overset{O}{S}CF_3$				81.25 (s)		5.22 (s)		

[a] The ^1H is relative to internal TMS; ^{19}F is relative to internal CCl_3F.

($R = CH_3, CF_3$) type compounds are somewhat more complex than the ABM_3X system of $FS(O)OCH_2CH_3$ because of the interactions of the CF_3 group. As would be expected, the coupling between the methylene protons remains essentially constant ($\Delta J_{AB} = 0.2$ cps) as do the methylene–methyl interactions ($\Delta J_{AM} = 0.1$ cps) when F is replaced by CF_3 in $FS(O)OCH_2CH_3$. Substitution of CF_3 by F is accompanied by a decrease of about 0.4 cps in the methylene proton–fluorine coupling. Replacing the ethyl group by 2,2,2-trifluoroethyl increases the degree of nonequivalence of the methylene protons ($\Delta J_{AB} = 2.6$ cps).

Surprisingly the J_{H-F} value of 1.2 cps remains unchanged when CF_3 is substituted for F in $FS(O)OCH_3$. This argues for "through-space" coupling, at least in the $CF_3S(O)-$ case, since if the splitting arises from a through-bond interaction in both cases, J should decrease for $CF_3S(O)-$ relative to $FS(O)-$.

Since the effect of the asymmetric center on magnetic equivalence is well established for $-S(O)O-$ systems, an examination of thiolsulfinates seemed appropriate. Unfortunately, it was not possible to synthesize the thio analogs and in every case a mixture of disulfides (CF_3SSR and RSSR) resulted. Other workers have suggested a mechanism for disulfide formation resulting from reactions of mercaptans with hydrocarbon thiolsulfinates which accounts adequately for the products observed in this case[14]



$$CF_3\overset{O}{S}F + RSH \longrightarrow CF_3\overset{O}{S}SR + HF$$

$$CF_3SOH + RSH \longrightarrow CF_3SSR + H_2O$$

Since large amounts of SiF_4 are observed as a reaction product, HF must accompany the initial formation of a thiolsulfinate. HF apparently does not participate further in the decomposition steps since the same products are observed in the presence of a base, either NaF or $(CH_3)_3N$. The postulated mechanism may also account for disulfide formation even when excess trifluoromethylsulfinyl fluoride is used because the thiolsulfinate ester would be hydrolytically less stable than $CF_3S(O)F$ or the disulfides. Thus, the mercaptan is regenerated and effectively consumes any excess $CF_3S(O)F$.

The disulfides are readily identified by infrared, mass,

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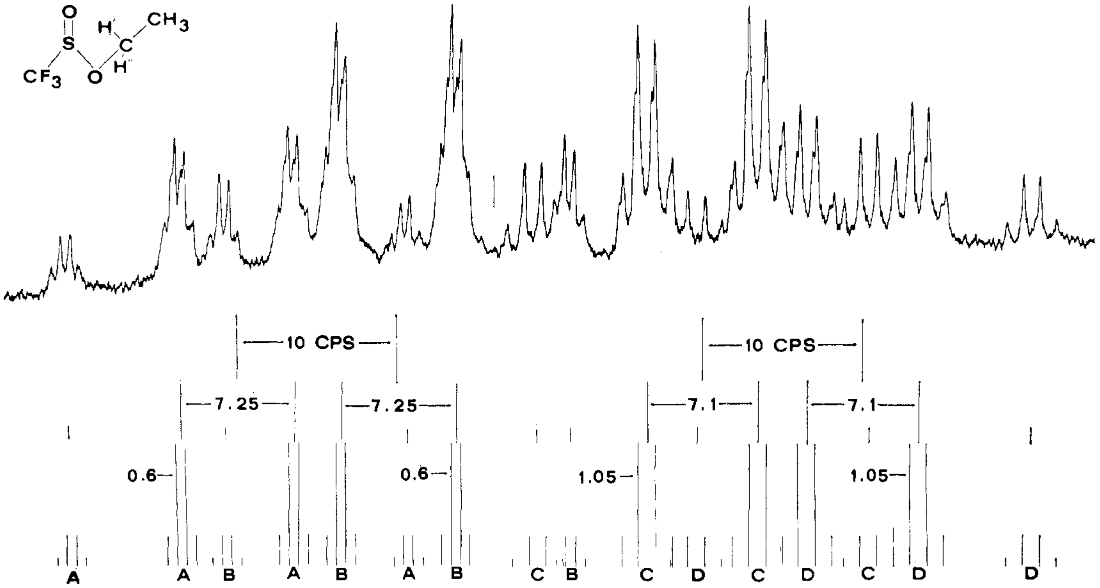

Figure 1.—Methylene proton nuclear magnetic resonance spectrum of $CF_3S(O)OCH_2CH_3$ recorded with a Varian HA-100 nmr spectrometer (50-cycle sweep).

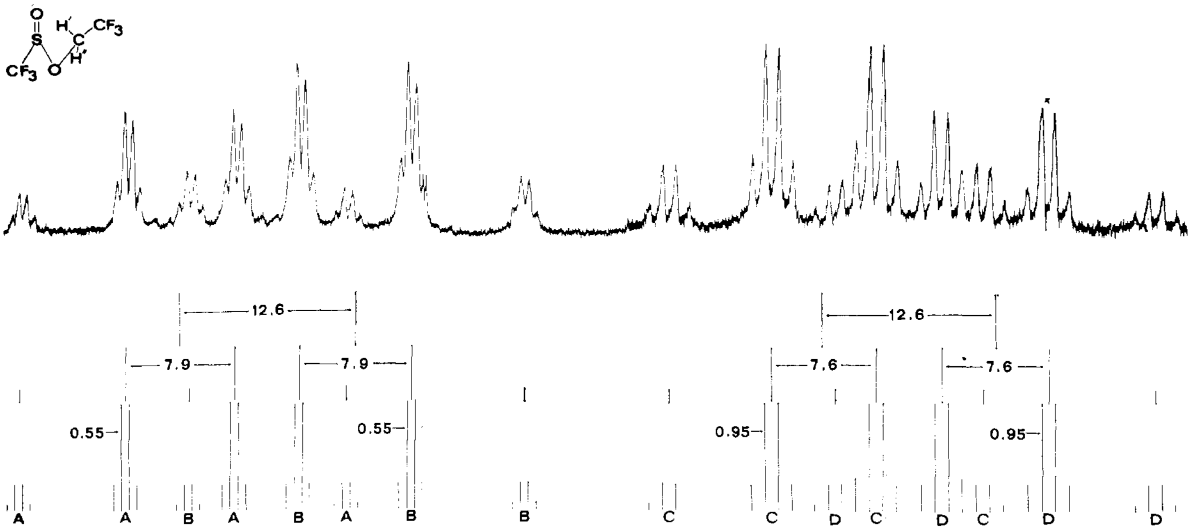

Figure 2.—Methylene proton nuclear magnetic resonance spectrum of $CF_3S(O)OCH_2CF_3$ recorded with a Varian HA-100 nmr spectrometer (50-cycle sweep).

and nmr spectra. The presence of CF_3S– or $CF_3S(O)$– is easily determined from nmr spectra since the fluorine resonance in the former occurs over the range 35–55 ppm and in the latter over the range 74–85 ppm.[4,6] Therefore, the resonance observed at 46.3 ppm in $CF_3SSC_2H_5$ can be assigned as CF_3S rather than $CF_3S(O)$–. Comparison with infrared spectra of known disulfides also substantiates this assignment.[15]

Trifluoromethylsulfinyl chloride with bis(trifluoromethylthio)mercury gives a mixture of bis(trifluoromethyl) disulfide and trifluoromethyl trifluoromethylthiosulfonate as identified by their infrared spectra.

$$CF_3S(O)Cl + Hg(SCF_3)_2 \longrightarrow$$

$$[CF_3\overset{O}{S}SCF_3] \longrightarrow CF_3SSCF_3 + CF_3SO_2SCF_3$$

Previous attempts to prepare $CF_3S(O)SCF_3$ have also resulted in the formation of CF_3SSCF_3 and $CF_3SO_2SCF_3$ with the thiolsulfinate postulated as an unisolable intermediate.[16] Similar disproportionations of hydrogenated thiolsulfinates have been reported.[17]

Reactions of $CF_3S(O)F$ with amines and ammonia give rise to perfluoroalkylsulfinamides, $CF_3S(O)NR_2$. These are colorless liquids of very low volatility where extrapolated boiling points occur in the range of 120–180° compared to those of the analogous sulfenamide compounds (50–100°). Higher boiling points coupled with Trouton constants which are also larger than those of the sulfenamides suggest a higher degree of association in the new molecules. The sulfinamides are thermally unstable above 100° and decompose in Pyrex to HCF_3, SO_2, OCS, and an unidentified nonvolatile dark residue. CF_3SSCF_3 is observed also in all cases except with $CF_3S(O)N(CH_2CH_3)_2$.

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TABLE II

INFRARED SPECTRA

$CF_3\overset{O}{S}OCH_3$	2960 w, 1461 w, 1209 vs, 1145 vs, 1000 sh, w–m, 972 s, 712 m, 608 w–m, 452 w
$CF_3\overset{O}{S}OCH_2CH_3$	2975 w, 1395 w, 1209 vs, 1147 vs, 1004 m, 900 s–vs, 721 m, 610 w–m, 460 w–m
$CF_3\overset{O}{S}OCH_2CF_3$	2975 w, 1450 w, 1410 w, 1295 s, 1221 vs, 1210 vs, 1185 vs, 1145 s, 1053 m, 1018 s–vs, 967 m, 850 w–m, 762 m-s, 656 w–m, 600 w–m, 550 w, 498 w, 454 w–m
$CF_3\overset{O}{S}N(CH_2CH_3)_2$	2982 w–m, 2945 w, 2885 w, 1738 w–m, 1463 w, 1385 w, 1201 vs, 1184 sh, s, 1164 sh, m, 1131 s, 1015 w, 917 w, 785 w, 667 w, 587 w, 430 w
$CF_3\overset{O}{S}N(CH_3)_2$	2945 w–m, 2904 w, 2947 sh, w, 2810 w, 1458 w, 1365 w, 1270 w–m, 1189 vs, 1130 vs, 1060 w, 943 s, 670 m, 585 w–m, 445 w–m
$(CF_3\overset{O}{S})_2NCH_3$	2942 vw, 1450 vw, 1208 vs, 1130 s–vs, 770 w–m, 732 w–m, 575 w, 475 w, 440 w
$CF_3\overset{O}{S}NH_2$	3438 vw, 3335 w, 1374 m, 1175 s, 1147 s, 1072 w, 738 m, 480 m, 421 w

TABLE III

ELEMENTAL ANALYSES AND VAPOR PRESSURE DATA

	Anal, %												Log P_{mm} = $A - B/T$		
	C		H		S		N		F			ΔS_v, eu			ΔH_v, kcal mol^{-1}
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Bp, °C		A	B	
$CF_3\overset{O}{S}OCH_3$	16.21	15.95	2.03	2.00	21.62	21.62			38.5	38.2	73	21.9	7.67	1656	7.6
$CF_3\overset{O}{S}OCH_2CH_3$	22.22	22.09	3.09	3.10	19.75	19.68			35.2	35.3	97	24.1	8.00	1893	8.9
$CF_3\overset{O}{S}OCH_2CF_3$	16.67	16.55	0.92	0.87	14.81	14.72			52.8	52.6	90	24.1	8.20	1931	8.8
$CF_3\overset{O}{S}N(CH_3)_2$	22.36	22.29	3.73	3.79	19.88	19.88	8.70	8.85	35.4	35.1	102 (510 mm)	24.6	7.73	1882	8.0
$CF_3\overset{O}{S}N(C_2H_5)_2$	31.74	31.57	5.31	5.38	16.93	16.84	7.42	7.51	30.2	30.2	109 (140 mm)	24.1	7.34	1988	10.7
$(CF_3\overset{O}{S})_2NCH_3$	13.68	13.46	1.14	1.23	24.43	24.57	5.32	5.44	43.3	43.2	118 (165 mm)	27.1	8.03	2275	12.0
$CF_3\overset{O}{S}NH_2$	9.12	9.12	1.54	1.47	24.06	24.02	10.52	10.42	42.8	42.3	92 (150 mm)	22.7	7.50	1943	9.6

Comparison of the methylene proton spectrum of $CF_3S(O)N(CH_2CH_3)_2$ with that of the ester $CF_3S(O)OCH_2CH_3$ shows that these protons are now equivalent or very nearly so ($J < 0.2$ cps). Equivalent methylene protons are observed in $FS(O)N(CH_2CH_3)_2$[3] but not in $CH_3OS(O)N(CH_2CH_3)_2$.[1] Since the CF_3 fluorine resonances are typically in the $CF_3S(O)$– region and no bands assignable to the asymmetric stretch of $O{=}\overset{|}{\underset{|}{S}}{=}O$ are observed in the infrared spectrum, the possibility of either CF_3S– or CF_3SO_2– amides is eliminated. A molecular ion minus CF_3 is found in the mass spectar of all the sulfinamides.

Experimental Section

Reagents.—Anhydrous methanol and ethanol, triethylamine, dimethylamine, and methylamine were purchased from Baker and Adamson. 2,2,2-Trifluoroethanol was obtained from Peninsular, ethanethiol from Aldrich, and methanethiol from Matheson. Trifluoromethylsulfinyl fluoride was prepared by the reaction of CF_3SSCF_3 (Peninsular) and AgF_2 (Ozark-Mahoning).[5] $Hg(SCF_3)_2$ was prepared by uv irradiation of CF_3SSCF_3 in the presence of mercury. All reagents were used as received without further purification.

Apparatus.—Infrared spectra were taken on a Perkin-Elmer Model 621 infrared spectrometer using a 10-cm gas cell with KBr windows and were calibrated against known absorption bands in polystyrene film. Proton and fluorine nmr were determined with a Varian HA-100 nmr spectrometer using tetramethylsilane and Freon 11 as internal standards. Mass spectra were obtained using a Hitachi Perkin-Elmer Model RMU 6E mass spectrometer. Beller Mikroanalytisches Laboratorium performed the elemental analyses.

Preparation of Sulfinyl Esters.—All of the esters were prepared in essentially the same manner. In a typical reaction, a 1.5:1 excess of $CF_3S(O)F$ was condensed into a vessel containing 3 mmol of the appropriate alcohol. The reactants were allowed to warm slowly from −78° to room temperature. The volatile esters were then isolated in quantitative yield from SiF_4 and excess $CF_3S(O)F$ by fractional condensation. $CF_3CH_2OS(O)CF_3$ and $CH_3OS(O)CF_3$ were stopped at −78° and $CH_3CH_2OS(O)CF_3$ at −63° while SiF_4 and $CF_3S(O)F$ passed into a −183° trap. These compounds are colorless liquids at 25°, are stable in Pyrex, and do not react with mercury. Infrared spectra are listed in Table II. Vapor pressure data and elemental analyses are given in Table III.

Reactions of $CF_2S(O)F$ with Mercaptans.—Regardless of reaction conditions, $CF_3S(O)F$ reacts with CH_3SH or C_2H_5SH to give a mixture of disulfides (RSSR and $RSSCF_3$) with no evidence for the thiolsulfinate $CF_3S(O)SR$. A 1.5–5-fold excess of $CF_3S(O)F$ condensed with either CH_3SH or C_2H_5SH neat or in the presence of a base, $(CH_3)_3N$ or NaF, resulted in the formation of disulfides. SiF_4 was observed when a base was not used to remove the HF formed. CF_3SSCH_3, $CF_3SSC_2H_5$, CH_3SSCH_3, and $C_2H_5SSC_2H_5$ were identified from their nmr, infrared, and mass spectra.

Reaction of $CF_3S(O)Cl$ and $Hg(SCF_3)_2$.—$CF_3S(O)Cl$ (1.5 mm) was condensed onto 1.7 mmol of $Hg(SCF_3)_2$. The mixture was allowed to warm to room temperature for 5 min. Infrared spectra of the volatile components showed a mixture of CF_3SSCF_3 and $CF_3SO_2SCF_3$ identified by comparison with known infrared spectra.

Preparation of Sulfinamides.—The general procedure for preparing the sulfinamides varied with the nature of the reactant used. $CF_3S(O)N(CH_3)_2$ and $CF_3S(O)N(CH_2CH_3)_2$ were prepared by treating $NH(CH_3)_2$ or $HN(C_2H_5)_2$ with $CF_3S(O)F$ in a 2:1 ratio by condensing 6 mmol of the appropriate amine with 3 mmol of $CF_3S(O)F$ into a Pyrex bulb and allowing the mixture to warm slowly to room temperature. The sulfinamides were trapped at −10 to −20° while any unreacted starting materials passed into a −183° trap.

$(CF_3S(O))_2NCH_3$ was prepared by treating $CF_3S(O)F$ (2 mmol) with NH_2CH_3 (1 mmol) in the presence of NaF and was purified by trap-to-trap distillation. When heated, it decomposes to COS, HCF_3, SO_2, and CF_3SSCF_3. $CF_3S(O)NH_2$ was prepared by reaction of a 10:1 mole ratio of NH_3 to $CF_3S(O)F$ at −40° for 2 hr and then allowing the vessel to warm slowly to room temperature. The product was purified by fractional condensation.

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Polyatomic Cations of Tellurium. I. The $+^1/_3$, $+^1/_2$, and +1 Oxidation States of Tellurium

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Tellurium dissolves in 45% oleum to give a yellow solution and in cold H_2SO_4 or HSO_3F to give red solutions which become orange-yellow on warming. It is shown that the red species is Te_4^{2+}. Tellurium can be oxidized with SbF_5, $S_2O_6F_2$, and AsF_5 to give the red compounds $Te_4(Sb_2F_{11})_2$, $Te_4(SO_3F)_2$, and $Te_4(AsF_6)_2$ which were also shown to contain Te_4^{2+}. With larger amounts of the appropriate oxidizing agents tellurium can be oxidized to the +1 oxidation state and the yellow compounds $TeSO_3F$ and $TeSbF_6$ have been prepared and characterized. It is shown that these tellurium(I) compounds and the yellow acid solutions contain a polyatomic cation Te_n^{n+} which is thought to be Te_4^{4+}. Using arsenic pentafluoride as an oxidizing agent, it was also possible to obtain tellurium in the $+^1/_3$ oxidation state in the form of the compound Te_3AsF_6 which is believed to contain the Te_6^{2+} cation.

In recent papers it has been shown that selenium forms the colored species Se_4^{2+} and Se_8^{2+} in strong acid solutions[1] and several compounds of these new cations have been described.[2,3] It has also been shown that sulfur can be oxidized to the colored cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+}.[4,5] Tellurium also forms orange or red solutions in sulfuric acid, oleum, or sulfur trioxide,[6,7] and a red compound "$TeSO_3$" has been described.[7-9] Indeed the reaction of tellurium with concentrated sulfuric acid to produce a red color was one of the first recorded properties of tellurium. The same red color has also been obtained by passing H_2Te through a saturated solution of TeO_2 in concentrated sulfuric acid and on continued passing of H_2Te it was reported that an insoluble brown substance was produced which did not appear to be elemental tellurium.[10] It seemed probable that these colored solutions of tellurium contain one or more polyatomic cations, analogous to those of selenium and sulfur, and this paper reports an investigation of solutions of tellurium in fluorosulfuric acid, sulfuric acid, and oleum and of the reaction of tellurium with the oxidizing agents $S_2O_6F_2$, SO_3, SbF_5, and AsF_5. Very recently Bjerrum and Smith[11] have shown that in $AlCl_3$–NaCl eutectic a red tellurium species is formed in maximum amount from Te and $TeCl_4$ at a mole ratio of 7. They concluded that the species contains tellurium in the $+^1/_2$ oxidation state and they formulated it as a polymeric cation Te_{2n}^{n+} formed according to the equation $7Te + Te^{4+} \rightarrow (4/n)Te_{2n}^{n+}$. They also obtained some evidence for another tellurium species with a formal oxidation state between $+^1/_2$ and 0, but this was not identified. Awad[12] has also postulated the existence of low-valency states of tellurium, *i.e.*, Te_2^+ and Te^+, in order to explain his results on the anodic dissolution of tellurium in nonoxidizing acids. Some of our results have been described in two preliminary publications.[13,14]

Results and Discussion

Tellurium dissolves slowly in cold sulfuric acid or fluorosulfuric acid to produce a red solution. With 45% oleum (disulfuric acid) the reaction is more rapid, and on warming the red oleum solution, a change to orange and finally to yellow occurs. A yellow-orange color is also produced on adding peroxysulfate to the red sulfuric acid solution or peroxydisulfuryl difluoride to the fluorosulfuric acid solution. On adding a large excess of these oxidizing agents, colorless solutions are produced, with precipitation of TeO_2 in the case of the sulfuric acid solutions. In the reaction of tellurium with sulfuric, fluorosulfuric, and disulfuric acids, sulfur dioxide is produced in all three cases. The colored tellurium species are, therefore, positive oxidation states of tellurium, the yellow species being in a higher oxidation

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