$$(C_2H_5)_4NCl\cdot HCl(s) + HCl(g) \longrightarrow (C_2H_5)_4NCl\cdot 2HCl(s) \qquad (2)$$

In order to eliminate the effect of possible $N—H\cdots S$ hydrogen bonding and with the hope of finding an equilibrium which would facilitate the determination of the hydrogen-bond energy in the $[HSHSH]^-$ species, the tetramethylammonium hydrosulfide–hydrogen sulfide system was investigated, with the results shown in Figure 2. Solid solution behavior is apparent up to the formation of the 1:1 adduct. A 3:1 adduct also forms. The variation of plateau pressure with temperature (48.718 cm at −45.5°, 12.729 cm at −63.5°, and 3.773 cm at −78.5°) allows the calculation of an enthalpy of −6.0 kcal/mole of H_2S absorbed for the reaction

$$(CH_3)_4NSH\cdot H_2S(s) + 2H_2S(g) \longrightarrow (CH_3)_4NSH\cdot 3H_2S(s) \qquad (3)$$

Again, this enthalpy change is identical in magnitude with that of the formally similar reaction[8]

$$(CH_3)_4NCl\cdot HCl(s) + 2HCl(g) \longrightarrow (CH_3)_4NCl\cdot 3HCl(s) \qquad (4)$$

From the similar enthalpy changes for similar reactions in the SH^-–H_2S systems and Cl^-–HCl systems it appears that the enthalpy change for the reaction

$$SH^-(g) + H_2S(g) \longrightarrow HSHSH^-(g)$$

might be as large as that for

$$Cl^-(g) + HCl(g) \longrightarrow ClHCl^-(g)$$

which has been found to be −14.2 kcal.[8] However, if one does not assume that the similarity in behavior of the two systems may be extrapolated to this point, then the lower limit for the hydrogen-bond energy in $HSHSH^-$ may be taken as 7 kcal/mole from the enthalpy change accompanying reaction 1. No structural studies have been carried out to establish whether the $SH^-\cdot(H_2S)_n$ species contain one or two hydrogen bonds per H_2S molecule adducted.

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Preparation and Properties of Some New Trifluoromethanesulfonates

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Nitrosyl trifluoromethanesulfonate, $NOSO_3CF_3$, has been prepared by the reaction of NO with $(CF_3SO_3)_2$ and quantitatively by the reaction of NOCl with CF_3SO_3H. Titanium tetrachloride reacts with CF_3SO_3H to yield the new compounds $TiCl_3(SO_3CF_3)$ and $TiCl_2(SO_3CF_3)_2$. X-Ray powder spectra and the Raman spectrum are presented for $NOSO_3CF_3$.

The reaction of peroxydisulfuryl difluoride, $S_2O_2F_6$, with nitric oxide to produce nitrosyl fluorosulfate[1] suggested that other peroxides might react similarly with nitric oxide. Bis(trifluoromethylsulfuryl) peroxide, $CF_3SO_2OOSO_2CF_3$, was found to react with nitric oxide at −78° to produce the new compound nitrosyl trifluoromethanesulfonate, $NOSO_3CF_3$. This material, a white hygroscopic solid, was also formed quantitatively by the reaction of excess nitrosyl chloride with trifluoromethanesulfonic acid at 25°. The Raman spectrum and relatively high melting point (170°) suggest that $NOSO_3CF_3$ may have considerable ionic character.

The fact that trifluoromethanesulfonic acid is known to liberate HCl from sodium chloride[2,3] suggested that other trifluoromethanesulfonates might be prepared by the reaction of trifluoromethanesulfonic acid with various chlorides. The reaction of CF_3SO_3H with excess $TiCl_4$ at 25° resulted in the formation of a hygroscopic, lemon-yellow solid having the composition $TiCl_3(SO_3CF_3)$. This compound decomposed when heated above 60° *in vacuo* according to the equation

$$2TiCl_3(SO_3CF_3) = TiCl_4 + TiCl_2(SO_3CF_3)_2$$

$TiCl_2(SO_3CF_3)_2$, a yellow solid resembling $TiCl_3(SO_3CF_3)$ in appearance, was also prepared by the reaction of $TiCl_4$ with excess CF_3SO_3H at 25°. The hygroscopic material was thermally stable to 222° at which temperature it melted with apparent decomposition. An attempt was made to produce a titanium compound containing more than two trifluoromethanesulfonate groups by heating a mixture of $TiCl_4$ and excess CF_3SO_3H, but no higher trifluoromethanesulfonate was isolated. These results are similar to those of Hayek, Puschman, and Czaloun,[4] who prepared $TiCl_2(SO_3F)_2$ by heating a mixture of $TiCl_4$ and excess HSO_3F. The compound was described as a lemon-yellow, hygroscopic solid thermally stable to 170°.

Experimental Section

Materials.—Trifluoromethanesulfonic acid was synthesized by the method of Haszeldine and Kidd.[5] This procedure involved the preparation of CF_3SO_2Cl by oxidation of CF_3SCl with excess Cl_2 in the presence of water. Small quantities of the reactants (3.5 g of CF_3SCl, 5.0 g. of H_2O, 5.0 g of Cl_2) were sealed in Pyrex glass ampoules and shaken vigorously for 7 days

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[1] J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 353 (1960).

[2] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 4228 (1954).

[3] R. E. Noftle and G. H. Cady, *Inorg. Chem.*, **4**, 1010 (1965).

[4] E. Hayek, J. Puschman, and A. Czaloun, *Monatsh.*, **85**, 359 (1954).

[5] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 2901 (1955).

in the dark. The CF_3SO_2Cl was separated from the reaction mixture by fractional condensation and hydrolyzed with $Ba(OH)_2$ to produce an aqueous solution of $Ba(SO_3CF_3)_2$. The solution was evaporated to dryness and the $Ba(SO_3CF_3)_2$ was extracted with and recrystallized from dry acetone. The purified salt was then dried at 140° for 6 hr under high vacuum. CF_3SO_3H was prepared by vacuum distillation from a mixture of dry $Ba(SO_3CF_3)_2$ and concentrated H_2SO_4. The product was redistilled and used without further purification. Purity was checked by comparing the infrared spectrum of a film of $CF_3SO_3H \cdot H_2O$ (produced when a sample of the acid was allowed to stand in air) with that of a standard spectrum obtained from the depository of The Chemical Society. CF_3SCl was obtained from Pierce Chemical Co., Rockford, Ill.

Bis(trifluoromethylsulfuryl) peroxide was prepared in small batches by electrolysis of CF_3SO_3H as described previously.[3] Such samples always contained a small amount of CF_3SO_3H as an impurity.

Nitrosyl chloride was prepared according to a method given by Brauer.[6]

Titanium tetrachloride of "purified quality" was obtained from Fisher Scientific Co., Fairlawn, N. J. It was transferred to a storage vessel under a blanket of dry nitrogen and pumped to remove HCl.

Nitrosyl trifluoromethanesulfonate, $NOSO_3CF_3$, was prepared in two ways. The first method involved the reaction of $CF_3SO_2OOSO_2CF_3$ with excess NO. Since only small quantities of the peroxide could be prepared at any one time and purification of the resulting product appeared difficult, a second method involving the reaction of CF_3SO_3H with excess NOCl was attempted. Pure $NOSO_3CF_3$ was prepared in this manner and, by comparison of X-ray powder patterns, was shown to be the same as the product obtained in the reaction of $CF_3SO_2OOSO_2CF_3$ with excess NO.

Method I.—A sample of bis(trifluoromethylsulfuryl) peroxide, unavoidably containing a small amount of CF_3SO_3H as an impurity,[3] was held in a reaction bulb at −196°. Excess NO (0.2623 g, 8.74 mmoles) was allowed to condense on top of the material, and the temperature of the vessel was raised to −78°. A white solid (later shown to be $NOSO_3CF_3$) was present at this time. The vessel was held at −78° for 12 hr and then allowed to warm slowly to 25° while open to a trap held at −183°. The volatile materials which condensed in this trap (0.3080 g) were analyzed by infrared spectroscopy and were shown to be NO (main component), NO_2, N_2O (very small amounts), $CF_3SO_3CF_3$, C_2F_6 (small amounts arising from partial decomposition of $CF_3SO_2OOSO_2CF_3$), and SiF_4 (trace).

The white solid (0.3004 g) remained behind in the reaction vessel and appeared to be stable at 25°. When this material was heated at 170° *in vacuo*, it evolved a gas shown to be primarily NO (a very small amount of SiF_4 was also present). In addition, a liquid of relatively low volatility was collected and shown to be CF_3SO_3H by infrared analysis (see Materials). Another sample of this white solid was allowed to come into contact with cold water. It hydrolyzed immediately producing a bluish solution. When air was allowed to enter the vessel, NO_2 was observed to form in the space above the liquid. This behavior indicated that the white solid was $NOSO_3CF_3$ contaminated with a small amount of CF_3SO_3H.

In a separate experiment, NO was allowed to condense in a bulb which contained CF_3SO_3H. The mixture was allowed to warm to −78° and remain at this temperature for 1 hr. Then the mixture was allowed to stand at room temperature for several hours. No white solid was observed indicating that the nitrosyl product was a result of the reaction between NO and $CF_3SO_2OOSO_2CF_3$ (not NO and CF_3SO_3H).

Method II.—Pure CF_3SO_3H (0.8904 g, 5.94 mmoles) was allowed to condense in a weighed 30-cc Pyrex glass bulb equipped with a Fisher and Porter 4-mm Labcrest-threaded glass valve and a Teflon-covered stirring bar. An excess of NOCl was then added at −196°. A reaction took place at −50° with the evolution of a gas (shown to be HCl by infrared analysis) and production of a white solid. The material volatile at −50° was transferred to another trap. NOCl (10 g, 133 mmoles) was added to the reaction vessel and the mixture was allowed to warm to room temperature. The reactants were stirred overnight by means of the magnetic stirring bar. After 12 hr the volatile materials were removed, and the product was pumped to constant weight. On the basis of the original weight of CF_3SO_3H, the weight of the product corresponded to 100.2% of that expected for $NOSO_3CF_3$ produced according to the equation

$$CF_3SO_3H + NOCl = NOSO_3CF_3 + HCl$$

In two separate experiments similar results were observed: calcd wt of product, 1.0625 and 2.1954 g; found, 1.0644 and 2.1941 g. In preliminary experiments, it was found that 100% weight uptake could not be achieved unless a large excess of NOCl was present. This result was probably due to better contact of the reactants since $NOSO_3CF_3$ is fairly soluble in NOCl.

Analysis.—Total nitrogen was determined in the following way. A sample of $NOSO_3CF_3$, which weight uptake data indicated to be pure, was hydrolyzed with 0.1 *N* NaOH containing an excess of 30% H_2O_2 (to oxidize all nitrogen species to NO_3^-).[1] The solution was then heated to decompose the excess H_2O_2, and nitrogen was determined on aliquots of this solution by the Devarda method.[7] *Anal.* Calcd for $NOSO_3CF_3$: N, 7.82. Found: N, 7.89.

$NOSO_3CF_3$ hydrolyzed vigorously in cold water to give initially a blue solution which slowly decolorized. It is postulated that basic hydrolysis of $NOSO_3CF_3$ proceeded according to the equation

$$NOSO_3CF_3 + 2OH^- = NO_2^- + CF_3SO_3^- + H_2O$$

(calcd mequiv of OH^-/mmole of $NOSO_3CF_3$, 2.000; found, 2.015). The presence of the trifluoromethanesulfonate ion in the hydrolysate was confirmed by ^{19}F nmr spectroscopy. The spectrogram for a solution obtained by dissolving $NOSO_3CF_3$ in water showed a single peak ($CF_3SO_3^-$) at 2.2 ppm upfield from an internal standard of CF_3COOH. A standard prepared by dissolving CF_3SO_3H and CF_3COOH in water gave an identical spectrum.

This mode of hydrolysis was consistent with those found for other nitrosyl compounds.[1,8]

X-Ray Spectra.—Powder spectra were obtained for samples of $NOSO_3CF_3$ prepared by methods I and II. The samples were ground, transferred to 0.2-mm Lindemann glass capillaries, and sealed with Halocarbon wax (series 6-00) in an oxygen-free drybox. The excess capillary was cut away with a microtorch outside the drybox. The samples were mounted in a standard Philips powder camera (57.3 mm) and exposed to nickel-filtered copper Kα radiation for 21–24 hr. Interplanar spacings were calculated from the observed values of 2θ taking film shrinkage into account. Data are presented in Table I. A comparison of the *d* values and intensities of the lines showed a good correspondence for the two samples and offered evidence that the materials were the same. The pattern obtained for $NOSO_3CF_3$ prepared by method I was somewhat diffuse and only 11 lines could be measured with accuracy. A doublet (3.84, 3.80) present on the pattern obtained for $NOSO_3CF_3$ prepared by method II was apparently unresolved on the first pattern.

Melting Point.—A pure sample of $NOSO_3CF_3$ was sealed in a melting point tube by the same method used for preparation of the X-ray samples. When the tube was heated slowly in a bath of concentrated H_2SO_4, the sample melted sharply at 170° to a yellow liquid. $NOSO_3CF_3$ sublimes slowly *in vacuo* at temperatures below its melting point.

Raman Spectrum.—Spectra were obtained using a Hilger

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(6) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. I, Academic Press Inc., New York, N. Y., 1963, p 512.

(7) N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., Princeton, N. J., 1939.

(8) W. J. Müller, D. M. Forbes, and R. Fort, *Angew. Chem.*, **45**, 782 (1932).

TABLE I

POWDER SPECTRA FOR $NOSO_3CF_3$[a]

d Spacings from Lines in X-ray Powder Photograph

Sample prepared by							
Method I		Method II		Method I		Method II	
d, A	Intens	*d*, A	Intens	*d*, A	Intens	*d*, A	Intens
		5.74	L			3.12	L
5.59	L	5.52	L			3.06	L
5.25	H	5.20	H	3.08	M	3.01	M
		5.05	L	2.97	L	2.97	L
		4.85	L			2.93	L
4.58	H	4.55	H	2.87	L	2.90	L
		4.25	L			2.76	L
4.19	M	4.19	M			2.70	L
3.84	H	3.84	H			2.66	L
		3.80	H			2.62	L
		3.67	L			2.58	L
3.61	L	3.64	L			2.51	L
		3.56	L			2.49	L
3.48	L	3.47	L			2.45	L
		3.40	L			2.44	L
3.34	L	3.35	L			2.41	L

[a] H, high; M, medium; L, low.

Model E 612 Raman spectrograph equipped with E 613 and E 614 cameras. A Toronto arc was used for excitation and spectra were recorded on Kodak spectroscopic plates, Type 11a-o. A solid sample of $NOSO_3CF_3$ gave a spectrum of four lines (cm^{-1}): 2230 s, 1224 b, 982 m, and 715 w. The most intense line (2230 cm^{-1}) was due to nitrosyl stretching and was in the range expected for a high degree of ionic character (NO^-) for the nitrosyl group.[9]

Trichloro(trifluoromethanesulfonato)titanium(IV).—In one experiment excess $TiCl_4$ (2.2809 g, 12.00 mmoles) was added to CF_3SO_3H (0.8597 g, 5.73 mmoles) contained in the 30-cc Pyrex glass reactor described previously. The vessel was allowed to warm from −183 to 25° whereupon a reaction took place with the evolution of a gas later shown to be HCl by infrared analysis. The only other volatile substance present was $TiCl_4$. On the basis of the original weight of CF_3SO_3H, the weight of the product corresponded closely to that expected for production of $TiCl_3(SO_3CF_3)$. Similar results were observed in two experiments: calcd wt of product if $TiCl_3(SO_3CF_3)$, 1.7372, and 1.7024 g; found, 1.7400 and 1.7000 g.

Dichlorobis(trifluoromethanesulfonato)titanium(IV).—Excess CF_3SO_3H (1.2355 g, 8.23 mmoles) was added to $TiCl_4$ (0.1730 g, 0.91 mmole) in the same manner as described above. A reaction took place on warming the vessel from −183 to 25° with the evolution of HCl. The reactants were stirred together overnight at 25°, and the product was then pumped to constant weight; calcd wt of product if $TiCl_2(SO_3CF_3)_2$, 0.3802 g; found, 0.3824 g.

Thermal Decomposition.—When a 1.6612-g sample of $TiCl_3(SO_3CF_3)$ was heated under vacuum, it began to evolve $TiCl_4$ when its temperature reached about 60°. The sample was held at 76° for 8 hr while pumping to constant weight. The $TiCl_4$ was collected in a trap held at −183° and later identified by its melting point. A pure sample of $TiCl_4$ and the unknown both melted near −23°. Apparently the decomposition followed the equation

$$2TiCl_3(SO_3CF_3) = TiCl_4 + TiCl_2(SO_3CF_3)_2$$

(calcd wt of product if $TiCl_2(SO_3CF_3)_2$, 1.1406 g; found, 1.1428).

Analysis.—Both $TiCl_3(SO_3CF_3)$ and $TiCl_2(SO_3CF_3)_2$ are lemon-yellow, very hygroscopic compounds. Analysis for titanium and chlorine was accomplished by conventional wet methods. In each case the compound was hydrolyzed with water in an evacuated bulb and washed into a beaker with 2 *N* HNO_3. NH_4OH (15 *M*) was then added to precipitate the hydrous oxide of titanium, and the solution was boiled to expel ammonia. The precipitate was separated by filtration, ignited, and weighed as TiO_2. The filtrate was diluted to the mark in a volumetric flask and after acidification, chloride was determined on aliquots of this solution by the Volhard method. *Anal.* Calcd for $TiCl_3(SO_3CF_3)$: Ti, 15.79; Cl, 35.08. Found: Ti, 16.1; Cl, 35.0. Calcd for $TiCl_2(SO_3CF_3)_2$: Ti, 11.49; Cl, 17.01. Found: Ti, 11.7; Cl, 16.8.

Melting Point.—A sample of $TiCl_2(SO_3CF_3)_2$ turned to a dark orange liquid containing bubbles in the vicinity of 222°.

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[9] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

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Reactions of Bromine(I) Fluorosulfate with Simple Inorganic Molecules and Polyfluoroolefins. A Novel Route to Perfluoro-2,3-butanedione

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Bromine fluorosulfate acts as a fluorosulfating agent with sulfur dioxide to give trisulfuryl fluoride, $S_3O_8F_2$. With phosphorus trifluoride, it is an oxygenating agent to give phosphoryl fluoride. Addition across double bonds of polyfluoroolefins occurs essentially quantitatively. The preparations of the compounds 2-bromo-3-fluorosulfatooctafluorobutane, 3-bromoheptafluoro-2-butanone, and 3-fluorosulfatoheptafluoro-2-butanone as intermediates in the synthesis of the diketone perfluoro-2,3-butanedione are discussed.

Bromine(I) fluorosulfate[1] is an easily prepared, high-boiling liquid which is stable in Pyrex under anhydrous conditions for several months. Gilbreath and Cady[2] have examined the reactions of $BrOSO_2F$ with C_2F_4 and

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[1] J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 352 (1960).

[2] W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2**, 496 (1963).