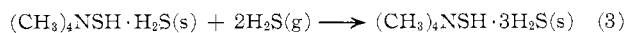
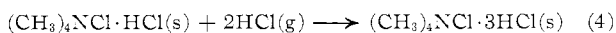


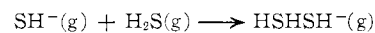
In order to eliminate the effect of possible N—H···S hydrogen bonding and with the hope of finding an equilibrium which would facilitate the determination of the hydrogen-bond energy in the $[\text{HSHSH}]^-$ species, the tetramethylammonium hydrosulfide–hydrogen sulfide system was investigated, with 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



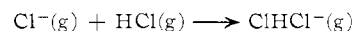
Again, this enthalpy change is identical in magnitude with that of the formally similar reaction⁸



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



might be as large as that for



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 $\text{SH}^-(\text{H}_2\text{S})_n$ species contain one or two hydrogen bonds per H_2S molecule adducted.

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Preparation and Properties of Some New Trifluoromethanesulfonates

By RONALD E. NOFTLE AND GEORGE H. CADY

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Nitrosyl trifluoromethanesulfonate, NOSO_3CF_3 , has been prepared by the reaction of NO with $(\text{CF}_3\text{SO}_2)_2$ and quantitatively by the reaction of NOCl with $\text{CF}_3\text{SO}_3\text{H}$. Titanium tetrachloride reacts with $\text{CF}_3\text{SO}_3\text{H}$ to yield the new compounds $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$ and $\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$. X-Ray powder spectra and the Raman spectrum are presented for NOSO_3CF_3 .

The reaction of peroxydisulfuryl difluoride, $\text{S}_2\text{O}_2\text{F}_6$, with nitric oxide to produce nitrosyl fluorosulfate¹ suggested that other peroxides might react similarly with nitric oxide. Bis(trifluoromethylsulfuryl) peroxide, $\text{CF}_3\text{SO}_2\text{OOS}_2\text{CF}_3$, 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 $\text{CF}_3\text{SO}_3\text{H}$ with excess TiCl_4 at 25° resulted in the formation of a hygroscopic, lemon-yellow solid having the composition $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$. This compound decomposed when heated above 60° *in vacuo* according to the equation



$\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$, a yellow solid resembling $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$ in appearance, was also prepared by the reaction of TiCl_4 with excess $\text{CF}_3\text{SO}_3\text{H}$ 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 $\text{CF}_3\text{SO}_3\text{H}$, but no higher trifluoromethanesulfonate was isolated. These results are similar to those of Hayek, Puschman, and Czaloun,⁴ who prepared $\text{TiCl}_2(\text{SO}_3\text{F})_2$ 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 $\text{CF}_3\text{SO}_2\text{Cl}$ 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

(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. Nofle 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 $\text{CF}_3\text{SO}_2\text{Cl}$ was separated from the reaction mixture by fractional condensation and hydrolyzed with $\text{Ba}(\text{OH})_2$ to produce an aqueous solution of $\text{Ba}(\text{SO}_3\text{CF}_3)_2$. The solution was evaporated to dryness and the $\text{Ba}(\text{SO}_3\text{CF}_3)_2$ was extracted with and recrystallized from dry acetone. The purified salt was then dried at 140° for 6 hr under high vacuum. $\text{CF}_3\text{SO}_3\text{H}$ was prepared by vacuum distillation from a mixture of dry $\text{Ba}(\text{SO}_3\text{CF}_3)_2$ 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 $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (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. $\text{CF}_3\text{SO}_2\text{Cl}$ was obtained from Pierce Chemical Co., Rockford, Ill.

Bis(trifluoromethylsulfuryl) peroxide was prepared in small batches by electrolysis of $\text{CF}_3\text{SO}_3\text{H}$ as described previously.³ Such samples always contained a small amount of $\text{CF}_3\text{SO}_3\text{H}$ 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_2CF_3 , was prepared in two ways. The first method involved the reaction of $\text{CF}_3\text{SO}_2\text{OOSO}_2\text{CF}_3$ 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 $\text{CF}_3\text{SO}_3\text{H}$ with excess NOCl was attempted. Pure NOSO_2CF_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 $\text{CF}_3\text{SO}_2\text{OOSO}_2\text{CF}_3$ with excess NO.

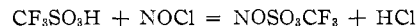
Method I.—A sample of bis(trifluoromethylsulfuryl) peroxide, unavoidably containing a small amount of $\text{CF}_3\text{SO}_3\text{H}$ as an impurity,³ was held in a reaction bulb at -196° . Excess NO (0.2623 g, 8.74 mmoles) was allowed to condense on top of the material, and the temperature of the vessel was raised to -78° . A white solid (later shown to be NOSO_2CF_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), $\text{CF}_3\text{SO}_2\text{CF}_3$, C_2F_6 (small amounts arising from partial decomposition of $\text{CF}_3\text{SO}_2\text{OOSO}_2\text{CF}_3$), 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 $\text{CF}_3\text{SO}_3\text{H}$ 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_2CF_3 contaminated with a small amount of $\text{CF}_3\text{SO}_3\text{H}$.

In a separate experiment, NO was allowed to condense in a bulb which contained $\text{CF}_3\text{SO}_3\text{H}$. 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 $\text{CF}_3\text{SO}_2\text{OOSO}_2\text{CF}_3$ (not NO and $\text{CF}_3\text{SO}_3\text{H}$).

Method II.—Pure $\text{CF}_3\text{SO}_3\text{H}$ (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

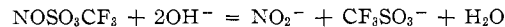
and a Teflon-covered stirring bar. An excess of NOCl was then added at -196° . A reaction took place at -50° with the evolution of a gas (shown to be HCl by infrared analysis) and production of a white solid. The material volatile at -50° was transferred to another trap. NOCl (10 g, 133 mmoles) was added 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 $\text{CF}_3\text{SO}_3\text{H}$, the weight of the product corresponded to 100.2% of that expected for NOSO_2CF_3 produced according to the equation



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_2CF_3 is fairly soluble in NOCl.

Analysis.—Total nitrogen was determined in the following way. A sample of NOSO_2CF_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_2CF_3 : N, 7.82. Found: N, 7.89.

NOSO_2CF_3 hydrolyzed vigorously in cold water to give initially a blue solution which slowly decolorized. It is postulated that basic hydrolysis of NOSO_2CF_3 proceeded according to the equation



(calcd mequiv of OH^- /mmole of NOSO_2CF_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_2CF_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 $\text{CF}_3\text{SO}_3\text{H}$ and CF_3COOH in water gave an identical spectrum.

This mode of hydrolysis was consistent with those found for other nitrosyl compounds.^{1,3}

X-Ray Spectra.—Powder spectra were obtained for samples of NOSO_2CF_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 K α 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_2CF_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_2CF_3 prepared by method II was apparently unresolved on the first pattern.

Melting Point.—A pure sample of NOSO_2CF_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_2CF_3 sublimes slowly *in vacuo* at temperatures below its melting point.

Raman Spectrum.—Spectra were obtained using a Hilger

(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).

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

TABLE I
POWDER SPECTRA FOR $\text{NOSO}_3\text{CF}_3^a$
 d Spacings from Lines in X-ray Powder Photograph

Sample prepared by							
Method I		Method II		Method I		Method II	
d , Å	Intens	d , Å	Intens	d , Å	Intens	d , Å	Intens
5.59	L	5.74	L			3.12	L
5.25	H	5.52	L			3.06	L
		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.

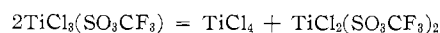
Model E 612 Raman spectrograph equipped with E 613 and E 614 cameras. A Toronto arc was used for excitation and spectra were recorded on Kodak spectroscopic plates, Type 11a-o. A solid sample of NOSO_3CF_3 gave a spectrum of four lines (cm^{-1}): 2230 s, 1224 b, 982 m, and 715 w. The most intense line (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 $\text{CF}_3\text{SO}_2\text{H}$ (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 $\text{CF}_3\text{SO}_2\text{H}$, the weight of the product corresponded closely to that expected for production of $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$.

(SO_3CF_3) . Similar results were observed in two experiments: calcd wt of product if $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$, 1.7372, and 1.7024 g; found, 1.7400 and 1.7000 g.

Dichlorobis(trifluoromethanesulfonato)titanium(IV).—Excess $\text{CF}_3\text{SO}_2\text{H}$ (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 $\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$, 0.3802 g; found, 0.3824 g.

Thermal Decomposition.—When a 1.6612-g sample of $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$ 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



(calcd wt of product if $\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$, 1.1406 g; found, 1.1428).

Analysis.—Both $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$ and $\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$ 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 $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$: Ti, 15.79; Cl, 35.08. Found: Ti, 16.1; Cl, 35.0. Calcd for $\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$: Ti, 11.49; Cl, 17.01. Found: Ti, 11.7; Cl, 16.8.

Melting Point.—A sample of $\text{TiCl}_2(\text{SO}_3\text{CF}_3)_2$ turned to a dark orange liquid containing bubbles in the vicinity of 222° .

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research. The authors wish to express their appreciation to Dr. Friedhelm Aubke and Professor R. J. Gillespie of McMaster University for the Raman spectra. They also thank B. J. Nist for the nmr spectra.

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

BY BOYD L. EARL, BRIAN K. HILL, AND JEAN'NE M. SHREEVE

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Bromine fluorosulfate acts as a fluorosulfating agent with sulfur dioxide to give trisulfuryl fluoride, $\text{S}_2\text{O}_3\text{F}_2$. 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) fluorosulfate¹ is an easily prepared, high-boiling liquid which is stable in Pyrex under anhydrous

conditions for several months. Gilbreath and Cady² have examined the reactions of BrOSO_2F with C_2F_4 and

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

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