bination and NSCl-producing reactions is the reaction of atomic nitrogen with $N \cdot S_2Cl_2$, then we predict the activation energy for the recombination reaction to be less than that for the NSCl-producing reaction. This prediction is in accord with the fact that the yield of NSCl, based on atomic nitrogen, was found to increase with increasing temperature.

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Preparation and Properties of Bis(trifluoromethylsulfuryl) Peroxide and Trifluoromethyl Trifluoromethanesulfonate

BY RONALD E. NOFTLE AND GEORGE H. CADY

Received March 4, 1965

Electrolysis of trifluoromethanesulfonic acid at −23° yields the unstable compound bis(trifluoromethylsulfuryl) peroxide, which decomposes explosively to perfluoroethane, sulfur trioxide, and the ester, trifluoromethyl trifluoromethanesulfonate.

The synthesis of peroxydisulfuryl difluoride, $S_2O_6F_2$, by electrolysis of fluorosulfuric acid[1] suggests that other new peroxides may be prepared by electrolysis of their corresponding strong acids. This suggestion was confirmed while this work was in progress by a report of the electrolytic preparation of dimethanesulfonyl peroxide, $(CH_3SO_3)_2$, from CH_3SO_3H.[2] When trifluoromethanesulfonic acid, CF_3SO_3H, was electrolyzed under high vacuum at about −23° in a cell similar to that described by Dudley,[1] the products obtained at the anode included bis(trifluoromethylsulfuryl) peroxide, $CF_3SO_2OOSO_2CF_3$. As a cold sample of this liquid compound was allowed to warm up, it decomposed suddenly[3] and with evolution of heat when its temperature reached about 10°. The products formed were perfluoroethane, sulfur trioxide, and the new ester, trifluoromethyl trifluoromethanesulfonate, $CF_3SO_3CF_3$. Although esters of trifluoromethanesulfonic acid containing hydrocarbon[4-6] and polyfluorohydrocarbon[7] groups have been reported, this ester appears to be the first instance of a perfluorocarbon trifluoromethanesulfonate. Trifluoromethyl trifluoromethanesulfonate is resistant to hydrolysis by water but does hydrolyze at 100° in 0.1 *N* sodium hydroxide.

The products observed from the decomposition of $(CF_3SO_3)_2$ can be explained on the basis of the following hypothetical mechanism

$$CF_3SO_3SO_3CF_3 \longrightarrow 2CF_3SO_3\cdot$$

$$CF_3SO_3\cdot \longrightarrow CF_3\cdot + SO_3$$

$$CF_3SO_3\cdot + CF_3\cdot \longrightarrow CF_3SO_3CF_3$$

$$2CF_3\cdot \longrightarrow C_2F_6$$

Experimental

Materials.—Trifluoromethanesulfonic acid was prepared by distillation from a mixture of barium trifluoromethanesulfonate[8] and concentrated sulfuric acid.[9] The product was redistilled and the fraction boiling near 56° under 15 mm. pressure was used.

Electrolysis.—The electrolysis cell employed for this work was similar in design to Dudley's cell C.[1] It was a small glass cell which could be cooled in a dewar vessel and operated under vacuum with separate collection of gaseous or volatile products from the anode and cathode. The cathode was a 1-cm. square piece of platinum foil, and the anode consisted of two 26 gauge platinum wires of 3 cm. length wound about each other. Since the conductivity of the pure trifluoromethanesulfonic acid was very low, a 0.1 *m* solution of sodium trifluoromethanesulfonate in trifluoromethanesulfonic acid was used. This was prepared by adding 0.202 g. of dry sodium chloride and 33.1 g. of trifluoromethanesulfonic acid to the cell, care being taken to exclude moisture from the system. The hydrogen chloride produced was pumped away. The cell was held at about −23° (to minimize transfer of the acid under vacuum) by a carbon tetrachloride slush bath, and the traps for collecting products were held at the boiling point of oxygen. When 36 volts was applied to the cell, a current of 0.014 amp. passed. A copper coulometer was used to measure the total charge passed.

While the cell was operating, a noncondensable gas was evolved at the cathode, and mass spectral analysis showed it to be hydrogen. No oxygen could be detected as a product at the anode. After about 10 hr. of steady operation, a blue color, also observed by Dudley, developed in the liquid occupying the cathode compartment of the cell. The liquid in the anode compartment remained colorless. In some runs the material in the anode trap was allowed to warm to room temperature while transferring the vapor to another trap at −183°. When the mixture of materials including trifluoromethanesulfonic acid approached about 10°, a sudden evolution of gas and heat was observed. The volatile products were separated by fractional codistillation[10] and each cut was analyzed by infrared spectroscopy.

The products were C_2F_6, $(CF_3)_2SO_3$, SO_3, and small amounts

---

(1) F. B. Dudley, *J. Chem. Soc.*, 3407 (1963).

(2) R. N. Haszeldine, R. B. Heslop, and J. W. Lethbridge, *ibid.*, 4901 (1964).

(3) Although the authors experienced no violent or destructive explosions due to the decomposition of $(CF_3SO_3)_2$ during the course of this work (possibly due to the fact that only small samples were prepared), larger samples might be expected to explode with considerable force, and caution should be exercised when working with this material.

(4) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(5) T. J. Brice and P. W. Trott, U. S. Patent 2,732,398 (1956).

(6) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).

(7) J. Burdon, *Tetrahedron*, 1 (1965).

(8) Gift from the Minnesota Mining and Manufacturing Co.

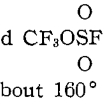
(9) J. M. Kidd and R. N. Haszeldine, *J. Chem. Soc.*, 4228 (1956).

(10) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

of COF_2, SO_2, trifluoromethanesulfonic anhydride,[5,6,11] and trifluoromethanesulfonic acid. At the cathode, the same products were observed by the same method of analysis, but were present in much lower yield except for SO_2 and CF_3SO_3H. Hydrogen was also liberated at the cathode but was not collected. It appeared to be the principal substance escaping from the cathode chamber of the cell. Assuming a two-electron charge to produce $(CF_3SO_3)_2$ at the anode, the current efficiency for a selected run was about 60%. This value was determined by measuring the total charge passed (0.91×10^{-2} f.) during electrolysis of a sample by means of a copper coulometer. The volatile products were collected, separated, and weighed. The total number of mmoles of $(CF_3)_2SO_3$ (1.81) plus the total number of mmoles of C_2F_6 (0.89) were taken to equal the number of mmoles of $(CF_3SO_3)_2$ (2.70) originally produced.

Bis(trifluoromethylsulfuryl) Peroxide.—Since the peroxide, $(CF_3SO_3)_2$, decomposed easily and was difficult to separate completely from CF_3SO_3H, no pure sample was obtained. In some runs decomposition of the material collected in the anode trap was avoided by handling it when in the solid or liquid state at temperatures below 0°. In spite of these difficulties, a chemical analysis was made in the manner now to be described: Before electrolysis was begun, 3 ml. of a 67% solution of sulfuric acid in water was placed in the anode trap to absorb SO_3 and CF_3SO_3H. After electrolyzing the acid under vacuum for 10 hr., the anode trap was held at about −70° and pumped to remove C_2F_6 and $(CF_3)_2SO_3$ as well as other volatile products. The trap was then warmed slowly to −10° and the product volatile at this temperature was pumped through a 22-cm. length of connecting glass tubing into a weighed bulb held at −183°. The bulb was then closed and allowed to warm slowly. The small amount of liquid present was observed to explode mildly when the temperature of the bulb reached about 10°. The bulb was again weighed (net wt. 0.3745 g. of product), the material was cooled to −183° (no O_2 was present),[12] and 5 ml. of distilled water was added. The volatile C_2F_6 and $(CF_3)_2SO_3$ were pumped off, separated from any water, and each weighed after separation by trap to trap distillation. The solution left behind was analyzed for SO_4^{2-} by precipitation as $BaSO_4$. The acid equivalents present were determined by titration with standard base. The analysis indicated a sample before decomposition to consist of 0.3332 g. of $(CF_3SO_3)_2$ and 0.0413 g. of CF_3SO_3H.

	Calcd. for above mixture	Found
Wt. of $(CF_3)_2SO_3$, g.	0.1648[13]	0.1648
Wt. of C_2F_6, g.	0.0500[13]	0.0500
Wt. of SO_3, g.	0.1184[13]	0.1204
Total g.-equiv. of acid	3.24×10^{-3}	3.22×10^{-3}

While this analysis shows the explosive material to be $(CF_3SO_3)_n$, it does not show n to equal 2. The conclusion that n equals 2 comes from the fact that the substance is colorless and, therefore, probably not the CF_3SO_3 free radical,[14] and from the fact that its volatility is apparently about the same as that of $(CF_3SO_2)_2O$, which boils at 84°. If n were 1, the boiling point should be about −10° (SO_3F_2 boils at −31° and  $CF_3O\overset{O}{\underset{O}{S}}F$ at −4°). If n were 3 the substance should boil at about 160° or more ($S_3O_8F_2$ boils at 120°) and should be approximately equal in volatility to CF_3SO_3H, which boils at about 162°. The method of preparation shows the new substance to be substantially more volatile than CF_3SO_3H. The fact that the substance gives a sharp n.m.r. spectrum in which all fluorine atoms are equivalent also shows that it is not a free radical (n is not 1) and that n is probably not more than 2. A molecule in which n is more than 2 would probably not have all CF_3 groups structurally equal.

Trifluoromethyl Trifluoromethanesulfonate.—A purified weighed sample of $(CF_3)_2SO_3$ was fused with potassium overnight at 450°. The excess potassium was destroyed with a small amount of ethanol, water was added, and the aqueous solution was analyzed for sulfide by adding an aliquot to an acidic standard potassium iodate–potassium iodide mixture. The excess iodine was back titrated with standard sodium thiosulfate solution. Fluoride was determined by steam distillation and subsequent titration with standard thorium nitrate solution. *Anal.* Calcd. for $(CF_3)_2SO_3$: S, 14.70; F, 52.27. Found: S, 15.1; F, 51.8.

The molecular weight obtained from vapor density measurements assuming ideal gas behavior was 217.8 ± 0.8 g./g.m.v. (average of four determinations); calcd., 218.1 g./g.m.v.

The melting point was determined by freezing a portion of a sample held in a 17-mm. o.d. glass tube. A large tube was used so that the sample could be observed directly from above while immersed in the cooling bath. The tube was allowed to warm in an n-butyl chloride bath at the rate of 0.4°/min., the temperature being measured by means of a calibrated thermocouple. Four determinations were made, each on a fresh portion of the sample. The solid was observed to start to melt at about −109°. The melting point was close to −108.2°.

Vapor pressures of $(CF_3)_2SO_3$ were measured in Pyrex glass apparatus similar to that described by Kellogg and Cady.[15] In this method the liquid was allowed to boil under various constant and measured pressures while the vapor was condensed in a reflux condenser at −78° and returned to the pot as a stream of liquid. The temperature corresponding to the equilibrium between liquid and vapor was measured by a copper–constantan thermocouple located about 10 cm. above the boiling liquid and 8 cm. below the condenser. Vapor pressures are shown in Table I. The approximate molar heat of vaporization at the boiling point was calculated to be 6.69 kcal./mole from the slope of the vapor pressure curve with the aid of the Clausius–Clapeyron equation. The boiling point was estimated to be 21.1° by extrapolation of the vapor pressure curve. These values lead to a Trouton constant of 22.7 e.u.

TABLE I

VAPOR PRESSURES OF $(CF_3)_2SO_3$

P, mm.	T, °K.	P, mm.	T, °K.	P, mm.	T, °K.
47	237.8	241	267.1	471	282.1
107	251.2	290	271.4	565	286.6
144	256.8	362	277.5	645	290.2
182	261.8	412	278.6	682	291.6
				732	293.5

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra were recorded using a Varian Model 4311B high resolution spectrometer with a 40-Mc. oscillator. Trichlorofluoromethane (Freon 11) was used as an external standard. Chemical shifts in p.p.m. relative to this standard were obtained for trifluoromethanesulfonic acid, +78.48 p.p.m., and trifluoromethanesulfonic anhydride, +74.02 p.p.m. The spectrum of trifluoromethyl trifluoromethanesulfonate first appeared as two separate peaks; one at +55.61 p.p.m. due to the CF_3 group attached to oxygen and one at +76.22 p.p.m. due to the CF_3 group attached to sulfur. Under high resolution these two peaks each split into a similar quartet having relative intensities 1:3:3:1. A spacing of 3.4 c.p.s. in the sharp quartets indicated this to be the spin–spin coupling constant between the two types of fluorine

---

(11) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

(12) On one occasion O_2 was observed as a product when a very impure sample of $(CF_3SO_3)_2$ decomposed. This result was not observed in subsequent experiments.

(13) Various proportions of these three substances could result from the decomposition of $(CF_3SO_3)_2$. The set given here was chosen to correspond to the observed amounts of C_2F_6 and $(CF_3)_2SO_3$ and from this the amount of SO_3 was calculated. The sum of the weights of the three substances, 0.3332 g., when subtracted from the total product, 0.3745 g., indicated 0.0413 g. of CF_3SO_3H. This plus 0.1184 g. of SO_3 corresponded to 3.24 mequiv. of acid.

(14) The free radical SO_3F is intensely colored like NO_2. See F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 3375 (1963).

(15) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

atoms in the F–C–S–O–C–F bond and space system. The decomposition of the peroxide, $(CF_3SO_3)_2$, was followed by n.m.r. spectrometry. When an impure sample of the peroxide which had been kept cold was scanned at low temperature in the C–F region, two large peaks were observed. The larger one at +77.19 p.p.m. could be ascribed to CF_3SO_3H while the smaller one at +72.36 p.p.m. could be ascribed to $(CF_3SO_3)_2$. Two small peaks were also observed for $(CF_3)_2SO_3$ at +54.66 and +75.30 p.p.m. as well as a trace peak for the anhydride of trifluoromethanesulfonic acid at +74.05 p.p.m. When the sample was taken out of the spectrometer and allowed to warm to room temperature, a reaction occurred in the tube with the evolution of heat. When the sample was again scanned in the C–F region, the spectrogram revealed that the peroxide peak had disappeared, the ester peaks had grown, and a new peak at +89.06 p.p.m. (attributable to perfluoroethane) had appeared. A rerun of the same sample when cold did not produce the original spectrum, but the ester and perfluoroethane peaks were enlarged still further due to the gas phase being more highly dissolved in the liquid phase at lower temperatures.

Mass Spectrum.—A Consolidated Engineering Corp. Type 21-103 mass spectrometer was used to record the mass spectrogram for $(CF_3)_2SO_3$, which showed peaks corresponding to the following ions in order of decreasing intensity: CF_3^+, SO^+, SO_2^+, CF^+, CF_2^+, COF^+, S^+, CF_3SO^+, COF_2^+, and $CF_3SO_2^+$. In addition, small peaks which could have been due to CF_3O^+, SO_3^+, and $CF_3SO_3^+$ were observed at about the same low intensity level as some impurity peaks in the mass spectrometer background. No peak corresponding to the molecule ion was noted.

Infrared Spectrum.—A Perkin-Elmer Model 21 infrared spectrometer with a sodium chloride prism was used to obtain the spectrum of $(CF_3)_2SO_3$ in the gas phase at 5 mm. pressure in a 10-cm. cell. Strong absorptions were found at 1461, 1258, 1230, 1134, and 954 cm.$^{-1}$. Two medium absorptions were noted at 786 and 766 cm.$^{-1}$. At 10 mm. pressure a weak band appeared at 868 cm.$^{-1}$. Some of these bands are close to those reported by Gramstad and Haszeldine for the S=O asymmetric vibration (1435 cm.$^{-1}$) and the S=O symmetric vibration (either 1227 or 1156 cm.$^{-1}$) in $CF_3SO_2CH_3$.[4]

Chemical Reactions.—An impure sample of $(CF_3SO_3)_2$ immediately liberated iodine from cold KI solution.

A sample of $(CF_3)_2SO_3$ was allowed to remain in contact with water at room temperature for 16 hr. The compound was immiscible and did not appear to react; sample wt. 0.7496 g., recovered 0.7291 g. Infrared analysis showed the recovered material to be the unchanged ester.

A sample of $(CF_2)_2SO_3$ was held in contact with 0.1 *N* sodium hydroxide at 100° for about 12 hr. (with occasional shaking). Then 5 ml. of a 5% $BaCl_2$ solution was added to precipitate barium carbonate. The excess base was titrated to the phenolphthalein end point and the milliequivalents of base used per milliequivalent of $(CF_3)_2SO_3$ calculated; calcd. mequiv. of base used per mmole of $(CF_3)_2SO_3$, 6.0; found, 5.7. Apparently the basic hydrolysis proceeded: $6OH^- + (CF_3)_2SO_3 = CF_3SO_3^- + 3F^- + CO_3^{-2} + 3H_2O$, but did not go to completion under these conditions.

Acknowledgment.—This work was performed in part with the support of a fellowship from the Allied Chemical Co. The authors thank the Minnesota Mining and Manufacturing Co. for furnishing the barium salt of trifluoromethanesulfonic acid. They also thank Mr. B. J. Nist for the n.m.r. spectra.

CONTRIBUTION FROM THE U.S. NAVAL ORDNANCE LABORATORY
CORONA, CALIFORNIA

Synthesis of a Cyclic Hexaphenyldichlorophosphonitrile Tetramer and Its Reactions with Diols

BY D. L. HERRING AND C. M. DOUGLAS

Received February 18, 1965

The reaction of sodium azide with a mixture of diphenylchlorophosphine and phenyldichlorophosphine yields hexaphenyldichlorophosphonitrile tetramer. This tetramer undergoes condensation with diols to form ring-linked polymeric products. The corresponding cyclic diphenoxy-, diethoxy-, and dihydroxyhexaphenylphosphonitrile tetramers are reported.

Introduction

The reaction of sodium azide with trivalent phosphorus halides has previously been employed in the synthesis of cyclic phosphonitriles. Diphenylphosphonitrile tetramer, $[(C_6H_5)_2PN]_4$, can be prepared by treatment of diphenylchlorophosphine with sodium azide at 220° followed by pyrolysis of the reaction products at 270°.[1] Phenyl chlorophosphonitrile tetramers, $[C_6H_5(Cl)PN]_4$, are formed from phenyldichlorophosphine and sodium azide at 165–170°.[2] While the bulk of the reaction mixture is composed of higher molecular weight species, two tetrameric compounds can be isolated. These isomers, m.p. 202 and 248°, have also been prepared by Shaw and Stratton *via* the reaction of phenyltetrachlorophosphorane and ammonium chloride.[3]

During our previous investigation of the reaction of iminobis(aminodiphenylphosphorane) chloride, $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$ (I), with phenyltetrachlorophosphorane, two hexaphenyldichlorophosphonitrile tetramers were prepared (m.p. 154–155 and 192–193°).[4] Based on the composition and most probable structure of I,[5] these compounds were believed to be *cis–trans* isomers of the following structure.

---

[1] D. L. Herring, *Chem. Ind.* (London), 717 (1960).

[2] D. L. Herring, unpublished results.

[3] R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 5004 (1962).

[4] D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **3**, 428 (1964).

[5] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *ibid.*, **1**, 84 (1962).