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The Chemistry of Sulfur Tetrafluoride. I. The Synthesis of Sulfur Tetrafluoride

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A convenient new synthesis of sulfur tetrafluoride has been discovered in the reaction of sulfur dichloride with sodium fluoride suspended in acetonitrile. Sulfur tetrafluoride also has been obtained by fluorinations of sulfur with chlorine and sodium fluoride or with iodine pentafluoride.

Recently sulfur tetrafluoride has been reported[1] to be a uniquely selective reagent which replaces carbonyl oxygen in aldehydes, ketones and carboxylic acids and forms the previously unknown organoiminosulfur difluorides by reaction with compounds containing carbon–nitrogen multiple bonds. Heretofore sulfur tetrafluoride has been difficultly accessible, but it has now been found that it can be prepared readily by the novel reaction of sodium fluoride with sulfur dichloride in refluxing acetonitrile and by fluorination of sulfur with chlorine and sodium fluoride or with iodine pentafluoride at elevated temperatures and pressures.

The previously known syntheses of sulfur tetrafluoride from sulfur and cobalt trifluoride[2] or elemental fluorine[3] give mixtures from which sulfur tetrafluoride can be isolated only with difficulty. Schmidt[4] has reported the synthesis of sulfur tetrafluoride by heating copper turnings with a yellow solid formed from iodine pentafluoride and sulfur monobromide. We have found that the reaction of iodine pentafluoride with sulfur monobromide proceeds at 200° under autogenous pressure to give sulfur tetrafluoride in 88% conversion without the use of copper turnings.

Synthesis from Sulfur Dichloride and Sodium Fluoride.—Sulfur tetrafluoride has been prepared routinely in the laboratory on a two-pound scale in 90% yield based on sulfur dichloride by treating the dichloride with excess sodium fluoride suspended in acetonitrile.

$$3SCl_2 + 4NaF \longrightarrow SF_4 + S_2Cl_2 + 4NaCl$$

The synthesis was accomplished by heating the reactants for 2 hours at 70–80° and atmospheric pressure in "Pyrex" glassware. The product was chiefly sulfur tetrafluoride (of 90% purity after a single distillation) which contained thionyl fluoride as a low-boiling contaminant. The distillation served to separate the sulfur monochloride formed as a coproduct of the oxidation–reduction reaction. Exploration of other reaction media indicated that liquids having a high dielectric constant, such as tetramethylene sulfone and benzonitrile, could replace acetonitrile. A search for other fluorides that would react with sulfur dichloride in acetonitrile or tetramethylene sulfone at 60–80° to give sulfur tetrafluoride showed potassium, cupric and zinc fluorides to be effective (see Table I).

Synthesis from Sulfur or Sulfur Chlorides, Chlorine and Sodium Fluoride.—Sulfur tetrafluoride also has been prepared in 70–90% yields based on sulfur or sulfur chloride by allowing chlorine in combination with sulfur, sulfur monochloride or sulfur dichloride to react with sodium fluoride at 200–300° under autogenous pressure.

$$S + 2Cl_2 + 4NaF \longrightarrow SF_4 + 4NaCl$$
$$S_2Cl_2 + 3Cl_2 + 8NaF \longrightarrow 2SF_4 + 8NaCl$$
$$SCl_2 + Cl_2 + 4NaF \longrightarrow SF_4 + 4NaCl$$

The highest yields were obtained with sulfur dichloride. The proportion of sulfur tetrafluoride in the product varied from 70–85% after one distillation. The main impurities were chlorine and thionyl fluoride (5–10%). The latter is presumed to have originated by adventitious hydrolysis of sulfur tetrafluoride. Since separation of thionyl fluoride from sulfur tetrafluoride is rather difficult, use of dry reactants and the exclusion of moisture from the reactor and containers for the sulfur tetrafluoride are important in minimizing the formation of this contaminant. Storage of chlorine-containing sulfur tetrafluoride over sulfur at room temperature and autogenous pressure converted the sulfur to sulfur monochloride which was separated by distillation. Both chlorine and thionyl fluoride present in crude sulfur tetrafluoride can be removed by distillation, but this procedure is wasteful of sulfur tetrafluoride which also distils in a ternary mixture (b.p. −48° to −46°) comprising 40 mole % SF_4, 40 mole % Cl_2 and 20 mole % SOF_2. Sulfur tetrafluoride boils at −38° to −37°.

Cesium and potassium fluorides reacted with chlorine and sulfur, or with chlorine and sulfur dichloride at 100 and 250°, respectively, forming sulfur tetrafluoride. Cupric fluoride, lead difluoride and barium fluoride also reacted with sulfur dichloride and chlorine at 325° to give sulfur tetrafluoride. Binary sulfides, such as potassium sulfide, ferrous sulfide and phosphorus pentasulfide, were found to be suitable sources of sulfur for these reactions and gave sulfur tetrafluoride in 45–80% yields, based on the sulfide, in reactions with sodium fluoride and chlorine at 225–235° (see Table II).

Synthesis from Sulfur and Iodine Pentafluoride.—An alternative sulfur tetrafluoride synthesis, which is simpler than that from sulfur and elemental fluorine,[3] has been found in the reaction of sulfur with iodine pentafluoride.[5] Stoichiometric amounts

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[1] W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt and D. D. Coffman, THIS JOURNAL, **81**, 3165 (1959).

[2] J. Fisher and W. Jaenckner, *Z. angew. Chem.*, **42**, 810 (1929).

[3] F. Brown and P. L. Robinson, *J. Chem. Soc.*, 3147 (1955), have reviewed the literature critically with respect to the preparation of SF_4 and describe a low temperature synthesis from sulfur and elemental fluorine.

[4] W. Schmidt, *Monatsh. Chem.*, **85**, 452 (1954).

[5] H. Moissan, *Compt. rend.*, **135**, 563 (1902). The reaction of sulfur with iodine pentafluoride was reported to give sulfur hexafluoride, but the reaction conditions were not cited. Under the conditions explored by us, no more than trace amounts of sulfur hexafluoride were detected in the reaction product.

TABLE I

SYNTHESIS OF SULFUR TETRAFLUORIDE AT ATMOSPHERIC PRESSURE FROM SULFUR DICHLORIDE, EMPLOYING A MEDIUM

Reactants (g.)	Medium (g.)	Reaction conditions	Product Yield,[a] %	 B.p., °C.	 Anal. (mole %)[c]
SCl_2 (146) NaF (150)	CH_3CN (176)	70–80° (1 hr.)	65[b]	−38 to −35	SF_4 (83–86) (MS) SOF_2 (13–14)
SCl_2 (73) NaF (75)	Tetramethylene sulfone (140)	48–71° (3 hr.)	46	−41	SF_4 (68–72) (MS) SOF_2 (22–24)
SCl_2 (73) KF (104)	CH_3CN (86)	50–72° (4.5 hr.)	43	....	SF_4 (53–58) (MS) SOF_2 (23–26)
SCl_2 (60) CuF_2 (49)	CH_3CN (132)	66–74° (3.5 hr.)	22	....	SF_4 (20) SOF_2 (65) (IR) SiF_4 (5–10)
SCl_2 (150) ZnF_2 (122)	CH_3CN (176)	61–78° (2.5 hr.)	45	...	SF_4 (45) SOF_2 (40) (IR) SiF_4 (<5)

[a] Includes SOF_2 believed to have been derived from SF_4 through hydrolysis by water adventitiously present. [b] See text of Experimental section for larger-scale preparation in approximately 90% yield. [c] MS, mass spectrometric analysis; IR, infrared analysis.

of these reactants were heated for 12 hr. at 100–300° under autogenous pressure. The sulfur tetrafluoride, which was separated from the co-product iodine and unreacted starting materials by distillation, was obtained in 84% yield and 90% purity, the major contaminant being thionyl fluoride.

Although sulfur tetrafluoride is susceptible to very rapid hydrolysis, it can be handled and manipulated in glass equipment provided the equipment has been thoroughly dried under vacuum. It is convenient to store this fluoride in stainless steel cylinders. The vapor pressure of sulfur tetrafluoride is about 10 atm. at 25°, and the critical temperature as measured by the disappearing meniscus method is 90.9 ± 0.2°.

Sulfur tetrafluoride has been found to be of the same order of toxicity as phosgene as judged by inhalation tests with animals.[6] The toxicity of sulfur tetrafluoride and the ease with which sulfur tetrafluoride hydrolyzes to hydrogen fluoride on contact with moisture make extreme precaution a prerequisite in working with this fluoride.

Experimental

Preparation of Sulfur Tetrafluoride from Sulfur Dichloride and Sodium Fluoride at Atmospheric Pressure.—A 12-liter, 4-necked "Pyrex" glass flask was provided with (1) a thermocouple well, (2) a 1-liter dropping funnel with a pressure equalizing line containing a stopcock and connections for evacuating the funnel and for drawing in sulfur dichloride from a reservoir, (3) a stirrer and (4) an upright, ice-cooled reflux condenser which exited by an inverted U-tube to a second upright condenser cooled by solid carbon dioxide-acetone to about −60°. The second (−60°) condenser exited to a receiver cooled in solid carbon dioxide. In an atmosphere of nitrogen the flask was charged with 2000 g. (48 moles, 20% excess) of powdered sodium fluoride and 6.5 liters of acetonitrile. The somewhat gelatinous mixture which resulted was stirred and heated to 68–70° and held at this temperature during the addition of 3100 g. (30 moles) of sulfur dichloride at the rate of 600 ml./hr. (4800 g. of a technical grade containing approximately 65% sulfur dichloride and 35% sulfur monochloride was satisfactory). The reaction was terminated 1.5 hr. after completing the addition of sulfur dichloride, during which time the reactants were kept at 70–72°.

The crude product, which distilled from the reaction mixture during the preparation, was collected in the receiver and cooled in solid carbon dioxide. The product consisted of an upper orange-yellow layer rich in sulfur tetrafluoride and a small lower red layer rich in sulfur dichloride. The condensate (originally 1200 g.) was subjected to three flask-to-flask distillations which effectively separated the higher-boiling sulfur dichloride. The more volatile sulfur tetrafluoride was collected in an evacuated and cooled (liquid nitrogen) 1-liter stainless steel cylinder equipped with a rupture disk and stored at room temperature. The 990 g. of crude sulfur tetrafluoride so obtained was shown by mass spectrometric analysis to contain on a molar basis 86–91% SF_4 and 8.5–12.5% SOF_2, corresponding to a 90% yield based on sulfur dichloride. Distillation of this material through a Podbielniak column gave 533 g. of heart cut, b.p. −38° to −37°, which was shown by mass spectrometric analysis to contain on a molar basis 94% SF_4 and 5% SOF_2. The distilled product was free of chlorine.

The use of sodium fluoride of correct particle size has been found to be important for best results in this synthesis. Sodium fluoride with particle size 50% in the 0.8–1.6 μ range and 50% in the 1.6–4.8 μ range was satisfactory. Commercial samples of Mallinckrodt or Baker and Adamson reagent grade sodium fluoride have ordinarily shown this general particle size range. In contrast, sodium fluoride with particle sizes 45% in the 1.6–6.4 μ, 45% in the 6.4–12.8 μ and 10% in the 12.8–49.6 μ range gave only a 39% yield of sulfur tetrafluoride. The sodium fluoride particle size was determined by microscopic examination.

Syntheses using tetramethylene sulfone rather than acetonitrile as medium and employing other metal fluorides are listed in Table I.

Preparation of Sulfur Tetrafluoride from Sulfur, Chlorine and Sodium Fluoride.—A 1-liter "Hastelloy C" shaker tube was charged with 32 g. (1.00 mole) of sulfur and 200 g. (4.76 moles) of sodium fluoride. After the tube had been cooled in solid carbon dioxide–acetone and evacuated, 142 g. (2.00 moles) of chlorine was added. The reactants were heated with rocking at 50° for 6 hr., at 100° for 2 hr., at 150° for 2 hr. and at 225° for 4 hr. The crude volatile materials, amounting to 100 g., were removed from the tube and distilled. There was obtained 94 g., b.p. −39° to −32°. This product was shown by infrared analysis to contain on a molar basis 80–85% SF_4 and 7.5–8.0% SOF_2, the remainder being chlorine. The analysis indicated an 82% yield of sulfur tetrafluoride, based on sulfur or chlorine. Chloride ion analysis of the sodium chloride–sodium fluoride mixture remaining in the tube after removal of sulfur tetrafluoride indicated an 80% yield.

A duplicate of this run at 290° for 1 hr. resulted in a 76% yield of sulfur tetrafluoride.

Preparation of Sulfur Tetrafluoride from Sulfur Dichloride, Chlorine and Sodium Fluoride.—A 1-liter "Hastelloy

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(6) The authors are indebted to the Haskell Laboratory for Toxicology and Industrial Medicine, E. I. du Pont de Nemours and Company, for the toxicological data.

TABLE II

SYNTHESIS OF SULFUR TETRAFLUORIDE

Reactants (g.)	Reaction conditions	Product		
		Yield,[a] %	B.p., °C.	Infrared analysis (mole %)
SCl_2 (77) Cl_2 (53) KF (208)	100° (2 hr.); 250° (4 hr.) 1-l. "Hastelloy C" shaker tube	46	Not dist.	SF_4 (20) SOF_2 (10) SiF_4 (5) HCl (5) Cl_2 (remainder)
S (3) Cl_2 (12) CsF (50)	100° (12 hr.) 200-ml. "Hastelloy C" shaker tube	25	Not dist.	SF_4 (30) SOF_2 (30) SiF_4 (10) HCl ($<$5) Cl_2 (remainder)
SCl_2 (30) Cl_2 (20) CuF_2 (75)	75° (2 hr.); 150° (1 hr.) 250° (1 hr.); 325° (2 hr.) 500-ml. "Hastelloy C" shaker tube	100	Not dist.	SF_4 (30) SOF_2 (30) HCl (10) SiF_4 (10) Cl_2 (remainder)
SCl_2 (52) Cl_2 (35) BaF_2 (190)	75° (1 hr.); 150° (1 hr.); 325° (4 hr.) 325° (4 hr.) 500-ml. "Hastelloy C" shaker tube	23	−30 to −40°	SF_4 (20) SOF_2 (20) SiF_4 ($<$5) Cl_2 (remainder)
S_2Cl_2 (67.5) Cl_2 (107) NaF (200)	50° (6 hr.); 100° (2 hr.); 150° (2 hr.); 225° (4 hr.) 1-l. "Hastelloy C" shaker tube	75	−43 to −38°	SF_4 (70) SOF_2 (5) Cl_2 (remainder)
K_2S (37) Cl_2 (71) NaF (56)	150° (2 hr.); 225° (8 hr.) 1-l. "Hastelloy C" shaker tube	80	Not dist.	SF_4 (40–45) SOF_2 (5) SiF_4 ($<$5) Cl_2 (remainder)
FeS (22) Cl_2 (62) NaF (90)	75° (1 hr.); 150° (1 hr.); 235° (6 hr.) 1-l. "Hastelloy C" shaker tube	51	Not dist.	SF_4 (10) SOF_2 (5–10) Cl_2 (remainder)
P_2S_5 (22) Cl_2 (106) NaF (160)	50° (2 hr.); 100° (2 hr.); 150° (2 hr.); 235° (4 hr.) 1-l. "Hastelloy C" shaker tube	45	Not dist.	SF_4 (35) SOF_2 (10) SiF_4 ($<$5) Cl_2 (remainder)

[a] Includes SOF_2 believed to have been derived from SF_4 through hydrolysis by water adventitiously present.

C" shaker tube charged with 103 g. (1.00 mole) of sulfur dichloride, 200 g. (4.76 moles) of sodium fluoride and 71 g. (1.00 mole) of chlorine was heated with rocking at 75° for 2 hr., at 150° for 2 hr. and at 250° for 2 hr. The crude volatile product, amounting to 114 g., was removed from the tube and distilled. There was obtained 105 g. of distillate, b.p. −38° to −34°. This product was shown by infrared analysis to contain on a molar basis 82–87% SF_4 and 7–7.5% SOF_2, the remainder being chlorine. The yield of sulfur tetrafluoride was 92% based on sulfur dichloride. Chloride ion analysis of the sodium chloride-sodium fluoride mixture formed during the run indicated a 95% yield, based on chlorine.

Preparation of Sulfur Tetrafluoride from Chlorine and Sulfur or Sulfur Dichloride and a Fluoride Other than Sodium Fluoride.—Several additional sulfur tetrafluoride syntheses using fluorides other than sodium fluoride in conjunction with chlorine and a source of sulfur were carried out as summarized in Table II. In these experiments, liquid or solid reactants were placed in the shaker tube under a nitrogen atmosphere, the head was assembled, the tube was cooled to solid carbon dioxide temperature, the nitrogen was removed with a vacuum pump and chlorine was condensed into the shaker tube. After being heated for the prescribed period, the shaker tube was allowed to cool to room temperature. The product was condensed into an evacuated stainless steel cylinder at liquid nitrogen temperature.

Preparation of Sulfur Tetrafluoride from Sulfur and Iodine Pentafluoride.—A 1-liter "Hastelloy C"-lined pressure vessel that had been flushed with nitrogen was charged with 87 g. (2.71 moles) of sulfur, and the bomb head and valve were attached. The reactor then was pressure-tested with nitrogen to 250 lb./sq. in., cooled in a solid carbon dioxide–acetone bath and bled to atmospheric pressure. The valve of the bomb then was removed, and iodine pentafluoride 479 g. (2.16 moles) was introduced through "Tygon" tubing which joined the cylinder of iodine pentafluoride with the nipple of the bomb head. The valve of the bomb was again attached, and the reactor was heated with agitation at 100° for 5 hr., then at 200° for 5 hr. and finally at 300° for 2 hr. The reactor then was cooled to room temperature, and the volatile material was distilled through a copper connecting tube into an evacuated stainless steel cylinder containing 30 g. of sodium fluoride pellets, the cylinder being cooled in a liquid nitrogen bath. The sodium fluoride pellets were employed to remove traces of hydrogen fluoride present. The crude volatile product obtained weighed 287.5 g. This product was combined with that from another run made under similar conditions in which 72.5 g. (2.26 moles) of sulfur and 400 g. (1.81 moles) of IF_5 reacted to give 219.5 g. of volatile product. On distillation of the volatile product in a low-temperature still, there was obtained 451 g. (83.9% yield) of SF_4, b.p. −38° (uncor.). Product prepared in this way was found by mass spectrometric analysis to contain about 93% sulfur tetrafluoride, the remainder being thionyl fluoride. The use of a large excess of either sulfur or iodine pentafluoride did not affect the course of the reaction.

Identification of and Analysis for Sulfur Tetrafluoride.—Sulfur tetrafluoride can be identified and its purity determined by either infrared[7] or mass spectrometric analysis. Each of these analytical procedures also can be used to determine the amount of thionyl fluoride present, but neither procedure is satisfactory for determination of the chlorine present.

The presence of chlorine in samples of sulfur tetrafluoride was detected qualitatively by passing a sample through aqueous potassium iodide solution. The development of an iodine color indicated the presence of chlorine. The presence of chlorine also was indicated if the sulfur tetrafluoride distillate was yellow, rather than colorless. A rough indication of the amount of chlorine present was the difference between 100% and the sum of the per cent. sulfur tetrafluoride and the per cent. thionyl fluoride found by spectral analyses.

The mass spectrum of sulfur tetrafluoride contains a weak peak for the molecular ion of mass number 108. The strongest peak results from the SF_3^+ ion; in addition, there is a very strong peak for the SF_2^+ ion and strong peaks for the SF^+ and F ions.

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(7) R. E. Dodd, L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).