infrared and mass spectrometric analyses were obtained they are indicated in the table and were in agreement with the structures of the products. The fluorine magnetic resonance spectra were obtained using a Varian high resolution n.m.r. spectrometer and electromagnet[12] at a frequency of 30 Mc. and a field of 7,500 gauss.

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(12) Varian Associates, Palo Alto, California.

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Chemistry of Sulfur Tetrafluoride.[1] V. Preparation of Sulfur Oxytetrafluoride and Sulfur Hexafluoride by Oxidation of Sulfur Tetrafluoride

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Sulfur oxytetrafluoride (SOF_4) was synthesized by the reaction of sulfur tetrafluoride (SF_4) with oxygen in the presence of catalytic amounts of NO_2 in high yield and conversion; this represents the first direct method for the preparation of SOF_4 not based on elemental fluorine. Oxidation of SF_4 with such inorganic oxides as NO_2, CrO_3 and CeO_2 gave sulfur oxytetrafluoride, sulfur hexafluoride and sulfuryl fluoride. Sulfur hexafluoride also was obtained by the microwave excitation of SF_4.

Introduction

Sulfur oxytetrafluoride (SOF_4) has been prepared previously only by the reaction of thionyl fluoride (SOF_2) with elemental fluorine.[2–4] Sulfur hexafluoride has been prepared generally by oxidative fluorination reactions based on elemental fluorine. In an investigation of the chemistry of sulfur tetrafluoride (SF_4), which can be prepared directly from sulfur dichloride and sodium fluoride in an acetonitrile medium,[5] it has been found that this compound can be oxidized to SOF_4 and SF_6 by several chemical methods.

Discussion

Oxidation of SF_4 with Nitrogen Oxides.—The nitrogen oxides and their salts are good reagents for effecting the oxidation of SF_4. The best oxidizing agents in this class are those in which the nitrogen atom is in a tripositive or higher oxidation state. Nitrogen dioxide, sodium nitrite and sodium nitrate were effective at 300°, but little or no oxidation occurred when SF_4 was heated with nitrous oxide or nitric oxide at this temperature. The formation of SOF_4 is favored at lower temperatures and lower SF_4 concentrations; SF_6 is the primary oxidation product at higher temperatures and with higher SF_4 concentrations. The effect of the SF_4 concentration can be seen from the idealized equations

$$2NaNO_3 + 6SF_4 \longrightarrow 5SOF_4 + SOF_2 + 2NaF + N_2 \quad (1)$$

$$2NaNO_3 + 11SF_4 \longrightarrow 5SF_6 + 6SOF_2 + 2NaF + N_2 \quad (2)$$

The use of $NaNO_3$ resulted in the formation of SOF_4 and SF_6 in yields of 57 and 20 mole %, respectively.

A volatile, reactive solid was obtained in all of the reactions in which nitrogen dioxide or nitrite or nitrate salts were employed for the oxidation of SF_4. This solid was shown to have the empirical formula $N_2O_3SF_5$, but the structure has not been determined. The solid dissociated reversibly at room temperature; one of the dissociation products was shown to be SOF_4, and the others contained NO groups as determined by mass spectrometric analysis. One method of representing the structure of this product would be $N_2O_2^+$-SOF_5^-, which is similar to $N_2O_2^+HSO_4^-$.[6] The formation of the SOF_5^- ion is not unreasonable, as cesium fluoride has been shown to combine with SOF_4 to give a reactive solid believed to be $CsSOF_5$. Such a simple formula probably is incorrect, however, as the presence of an $N_2O_2^+$ ion having an unpaired electron would be expected to impart color to the product. It is suggested that the actual structure may involve the SOF_5^- ion together with a positive ion or ions containing only nitrogen and oxygen in which all of the electrons are paired.

Catalytic Oxidation of SF_4 with Oxygen.—Sulfur tetrafluoride does not react with oxygen at 300°, but in the presence of NO_2 as catalyst sulfur(VI) fluorides were obtained in high yields and conversions. This method proved particularly valuable as a route to SOF_4; at 200° SOF_4 was obtained routinely in 75–80% yield and conversion. The amount of oxygen employed was at least equivalent to the amount of SF_4 used but could be present in excess without adversely affecting the yield of SOF_4. The reaction may be run at temperatures as low as 140°, but at this temperature a longer reaction period is required and the yield is less satisfactory as thionyl fluoride is formed in higher concentrations.

The oxidation process is presumed to involve the oxidation of SF_4 by NO_2 to give SOF_4 and NO. The NO is then assumed to undergo oxidation by oxygen to regenerate NO_2. This reaction mechanism is supported by the experimental observations:

(1) SF_4 does not react with oxygen alone at temperatures up to 300°.

(2) The reaction of SF_4 and NO_2 at 200° gives NO as the principal reduction product.

(3) The moderately rapid, reversible reaction of NO and oxygen to give NO_2 takes place in the

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(1) Paper IV, A. L. Oppegard, W. C. Smith and V. A. Engelhardt THIS JOURNAL, **82**, 3835 (1960).

(2) W. Kwasnik, "Inorganic Chemistry," Vol. I, 1948, pp. 192–193.

(3) H. Jonas, *Z. anorg. allgem. Chem.*, **265**, 273 (1951).

(4) F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., THIS JOURNAL, **78**, 290 (1956).

(5) Paper I, C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *ibid.*, **82**, 539 (1960)

(6) F. Seel, B. Ficke, L. Riehl and E. Volkl, *Z. Naturforsch.*, **8B**, 607 (1953).

gas phase at the reaction temperatures employed and the equilibrium lies to the right.[7]

Oxidation of SF_4 with Metal Oxides.—The oxidation of SF_4 to sulfur(VI) fluorides also has been accomplished with a number of metal oxides. The oxides which effect the oxidation of SF_4 are those whose corresponding fluorides are either good oxidizing agents themselves or are unknown.[8] Both binary and ternary oxides were employed as oxidizing agents, and of these the most effective were chromium(VI) oxide and the alkali metal chromates.

This method suffers from the disadvantage that the fluorine of the SF_4 is inefficiently converted to SOF_4 and SF_6; a considerable amount of fluorine combines with the metal to form metal fluorides and/or oxyfluorides. Thionyl fluoride is a major constituent of the volatile product and cannot be removed completely by distillation.

Pyrolysis of SF_4.—The very high thermal stability of sulfur tetrafluoride has been demonstrated in pyrolysis studies.[9] At 500–1000° and contact times of several hours less than 1% conversion of SF_4 to SF_6 takes place. Equilibria data for the reaction

$$3SF_4 \rightleftarrows 2SF_6 + S$$

are consistent with these experimental results in that the calculated equilibrium constants in the temperature range 500–1000° are very small.[10] The experimental details of this work have been described elsewhere.[9]

In contrast to thermal pyrolysis it has been found that microwave excitation of SF_4 leads to SF_6 in about 59% conversion and 80% yield. The energies involved in this method are very large, and SF_4 probably undergoes nearly complete dissociation into S and F· under these conditions. Recombination of these atomic species under non-equilibrium conditions then would lead to the preferential formation of SF_6. Such a process is, at least formally, analogous to the reaction of sulfur with elemental fluorine.

It is also of interest to note that electrolysis of SF_4-liquid hydrogen fluoride solutions has produced SF_6 with an over-all current efficiency of 70%.[11] The reaction is represented by the equation

$$SF_4 + 2HF \xrightarrow{\text{electrolysis}} SF_6 + H_2$$

It is therefore apparent that the conversion of SF_4 to SF_6 in high yield and conversion can be accomplished only if sufficiently high energy sources are provided.

Experimental

Preparation of SOF_4 from Sulfur Tetrafluoride and Oxygen in the Presence of Nitrogen(IV) Oxide as Catalyst.—Reactions were carried out in 400-ml. stainless steel pressure vessels. As SOF_4 was the product particularly desired, no attempt was made to recover the more volatile SF_6 quantitatively. In a typical experiment 108 g. (1.00 mole) of SF_4, 16.0 g. (0.50 mole) of oxygen and 9.0 g. (0.21 mole) of NO_2 were heated at 200° for $7\frac{1}{3}$ hours. The bomb was bled to atmospheric pressure through a trap cooled in solid carbon dioxide–acetone. The liquid condensed in the trap (108 g.) was transferred to a cylinder cooled in liquid nitrogen; the small amount of less volatile solid product was discarded. Mass spectrometric analysis of the product in the liquid phase showed that it contained 86.0% SOF_4, 8.7% SOF_2, 2.5% SO_2F_2, 1.4% NO and/or NOF, and trace amounts of SF_6, N_2O, SiF_4, N_2 and O_2; no SF_4 was present. The yield of SOF_4 was 80% based on the mass spectrometric data and the SF_4 employed in the reaction.[12]

All of the major impurities in the SOF_4 except SO_2F_2 were removed from the crude product by selective absorption in dimethylformamide.[13] In a typical purification 85 g. of crude SOF_4 was scrubbed twice with 50-ml. portions of dimethylformamide; this was done by condensing the crude SOF_4 in a cylinder containing the dimethylformamide and allowing the cylinder to stand for one-half hour at room temp. In the first wash 11 g. of material was dissolved by the solvent and in the second an additional 2 g. was removed. Mass spectrometric analysis of the purified product showed that it contained only SOF_4 (96.5 mole %), SO_2F_2 (3 mole %) together with minor amounts of nitrogen (0.3 mole %) and SiF_4 (0.2 mole %). The composition of the scrubbed material also was confirmed by infrared[14] and nuclear magnetic resonance[15] analyses.

There was no reaction between SF_4 and oxygen alone under comparable conditions. Nitrogen(II) oxide reacted with SF_4 to only a slight extent even at 300°. At this temperature with a reaction period of 9 hours the yields of SOF_4 and SF_6 were 5 and 1%, respectively.

Oxidation of SF_4 with Nitrogen(IV) Oxide.—An 80-ml. stainless steel-lined bomb charged with 4.6 g. (0.10 mole) of nitrogen dioxide (NO_2) and 44 g. (0.40 mole) of SF_4 was heated at 200° for 2 hours, at 250° for 2 hours, and then at 300° for 8 hours. A volatile product, weighing 38.0 g., was transferred to a cylinder cooled in liquid nitrogen. A yellow solid, weighing 2.4 g., which reacted vigorously with water and formed brown fumes when exposed to the atmosphere, also was obtained. Mass spectrometric analysis of the volatile product in the liquid phase showed that it contained 7% SOF_4, 5% SF_6, 2% sulfuryl fluoride (SO_2F_2), 21% SF_4, and 44% elemental nitrogen. Calculations based on these data showed that the yields of SOF_4 and SF_6 were 19 and 14%, respectively.

The reactive solid product described above was obtained as a major product when the reaction was carried out at a lower temperature with equivalent amounts of the reactants. A bomb charged with 23 g. (0.50 mole) of NO_2 and 54 g. (0.50 mole) of SF_4 was heated at 150° for 14 hours. The bomb was bled to atmospheric pressure through a trap cooled in acetone–solid carbon dioxide and both liquid and solid products were collected in the trap. The condensed liquid was transferred to a cylinder cooled in liquid nitrogen; this product, which weighed 38 g., was shown by mass spectrometric analysis to contain in mole % 50, SOF_2; 21, SO_2F_2; 7, unreacted SF_4, about 1 mole % each of SF_6, SOF_4, nitrogen and about 15 mole % of a species that yielded the NO fragment in the spectrometer. The solid product was allowed to warm up until it apparently was free of liquid and was colorless; it weighed 36.2 g. This product volatilized on warming but could be stored indefinitely at acetone–solid carbon dioxide temperatures without change. This oxygen- and moisture-sensitive solid was shown by elemental analysis to have the empirical formula $F_5N_2O_3S$; it was identical with the by-product obtained from the reaction of $NaNO_3$ with SF_4.

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(7) W. F. Glauque and J. D. Kemp, *J. Chem. Phys.*, **6**, 40 (1938); E. Briner, W. Pfeiffer and G. Malet, *J. chim. phys.*, **21**, 25 (1924).

(8) Paper IV (ref. 1); metal oxides whose corresponding fluorides are not strong oxidizing agents are converted to these fluorides by treatment with SF_4, and no oxidation takes place.

(9) E. L. Muetterties, U. S. Patent 2,883,267, April 21, 1959.

(10) J. D. Vaughan and E. L. Muetterties, unpublished results.

(11) E. H. Man, U. S. Patent 2,904,476, September 15, 1959.

(12) Preliminary work dealing with this synthesis has appeared elsewhere (W. C. Smith, U. S. Patent 2,907,636, October 6, 1959).

(13) The authors are indebted to Dr. R. D. Cramer for the purification procedure.

(14) F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., This Journal, **78**, 1553 (1956).

(15) F. B. Dudley, J. N. Shoolery and G. H. Cady, *ibid.*, **78**, 568 (1956).

TABLE I

OXIDATION OF SF_4 WITH SELECTED OXIDES

Solid reactant					Products			
							Oxidation products[a]	
Oxide	Mole	SF_4, Mole	Temp., °C.	Time, hr.	Solid, g.	Gas, total wt. (g.)	Compound	Yield (%)[b]
CrO_3	0.20	0.60	100	2	23 (tan)			
			200	4		59.6	SOF_4	46
			300	6			SF_6[c]	16
CrO_3	.20	.81	As above		23 (tan)[d]	76.0	SOF_4	25
							SF_6[e]	46
Na_2CrO_4	.10	.37	As above		18.8 (pale green)	34.0	Moderate amts. SOF_4, SO_2F_2[f]	
$K_2Cr_2O_7$	.10	.71	[g]		33.0	72.0	Moderate amts. SF_6, SO_2F_2[h]	
MnO_2	.15	.6	300	2	12[j]	66.0	Small amts. SOF_4, SF_6[k]	
			350[i]	12				
CeO_2	.20	.61	100	2	34[m]	54.3	Small amts. SO_2F_2, trace SF_6[n]	
			135[l]	(flash)				
PbO_2	.15	.42	100	2	31.5[p]	43.5	Traces SOF_4, SF_6, considerable oxygen[q]	
			200	4				
			300	6				
$NaNO_2$	.20	.76	200	2	9.5 (colorless	85.0	SOF_4	8
			250	2			SF_6[r]	42
			300	8				
$NaNO_3$	.10	.48	As above		3.9 (colorless)	55.0	SOF_4	57
							SF_6[s]	20

[a] Yields calculated from mass spectrometric data and based on idealized equations. Based on metal oxide. [c] Product contained: 22% SOF_4; 5% SF_6; 10% SO_2F_2; 57% SOF_2 and 5% SF_4. [d] Solid product contained 37.12%, chromium, 60.50 fluorine, and 3.89% sulfur; X-ray analysis indicated it was amorphous. [e] Product contained (/): 10% SOF_4; 12% SF_6; 9% SO_2F_2; 67% SOF_2 and 2% SF_4. [f] Product contained: 7% SOF_4; 0.3% SF_6; 7% SO_2F_2; 52% SOF_2 and 20% SF_4. [g] On rising temperature, an exothermic reaction occurred at 290° and temperature rose to over 400°. No further heating employed. [h] Product contained 13.5% SF_6; 18% SO_2F_2; 59% SOF_2 and 5.9% SF_4; only a trace of SOF_4. [i] No reaction at 300° after 6 hours. [j] X-Ray showed product was primarily MnF_2, but contained small amount of MnO_2. [k] Product contained: 3% SOF_4; 5% SF_6; 1% SO_2F_2; 50% SOF_2; 40% SF_4. [l] On heating reactants above 100°, flash from 135–180° recorded; no further heating employed. [m] X-Ray pattern in good agreement with that of CeF_3. [n] Product contained: 0.5% SF_6; 4% SO_2F_2; 42% SOF_2; 54% SF_4; oxygen observed on upright sampling. [p] X-Ray pattern that for PbF_2 containing small amount of PbO_2. Calcd. for PbF_2: Pb, 84.50; F, 15.50. Found: Pb, 81.72; F, 12.16. [q] Product contained: 0.3% SOF_4; 0.1% SF_6; 29% SOF_2; 67% SF_4; oxygen (1% in liquid phase, 16% in vapor phase). [r] Product contained: 3.5% SOF_4; 10% SF_6; 49% SOF_2; 31% SF_4. [s] Product contained: 27% SOF_4; 5.2% SF_6; 1% SO_2F_2; 27% SOF_2; 35% N_2; 1% NO. Also isolated small amount of colorless volatile solid similar to that obtained in NO_2–SF_4 reaction.

Attempts to characterize the solid material further met with only limited success. The solid decomposed in efforts to effect solution in a variety of organic solvents. Contact with dry air resulted in the rapid formation of brown fumes. Mass spectrometric studies showed that the solid dissociated on warming to give SOF_4 as the only sulfur-containing species together with one or more compounds having an NO^+ fragment ion.

Calcd. for $F_6N_2O_3S$: F, 46.78; N, 13.75; S, 15.79. Found: F, 46.39; N, 13.47, 13.95; S, 16.12.

Oxidation of SF_4 with Selected Oxides and Salts.—Reactions were carried out in 145-ml. "Hastelloy"-lined pressure vessels that were agitated during the reaction period. The oxide or salt was charged into the bomb, the latter was cooled in an acetone–solid carbon dioxide bath and the desired amount of SF_4 was weighed in. Volatile products were collected in stainless-steel cylinders cooled in liquid nitrogen and analyzed by mass spectrometric analysis in the liquid phase. Solid products were removed from the reactor and transferred under a blanket of nitrogen to polythene bottles.[16]

The experimental results are summarized in Table I. The effect of the reactant ratio on the ratio of SOF_4 and SF_6 in the volatile product is seen from a study of the CrO_3–SF_4 reaction. The nitrite and nitrate salts and the chromium (VI) oxides are effective reagents for the oxidation of SF_4 but the other oxides investigated were poor in this respect.

Microwave Excitation of SF_4.[17]—The apparatus and procedure were similar to those described in the literature,[18] the only difference being the use of an alumina liner in the reactor. In one experiment SF_4 (*ca.* 0.1 g./min.) and N_2 (*ca.* 0.2 g./min.) were passed through the reaction zone at a total pressure of 4 mm. for thirty minutes. The condensable products were trapped at the exit of the reactor on a liquid nitrogen-cooled cold finger. The product (2.3 g.) collected on the cold finger was transferred to a stainless-steel cylinder. Mass spectrometric analysis of this material at 25° showed that it contained 53% SF_6; 28% SF_4; 13% SOF_2; 2%, SiF_4; 1% SO_2; 0.2% SOF_4. The yield of SF_6 based on this analysis was 80% and the conversion 59%.

Acknowledgments.—The authors are indebted to Drs. E. H. Man, E. L. Muetterties and W. D. Phillips for their contributions to this work.

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(16) Several early experiments dealing with this study have been described previously (W. C. Smith, U. S. Patent 2,904,398, September 15, 1959).

(17) The authors are indebted to Dr. C. S. Cleaver for this experiment.

(18) R. L. McCarthy, *J. Chem. Phys.*, **22**, 1360 (1954).