the proposed bridge structure for dibutyltin iron tetracarbonyl and its homologs each iron atom has a *pseudo*-inert gas structure. Although the experimental data do not absolutely rule out an alternative bridge structure involving tin–tin and iron–iron bonds as well as tin–iron bonds, this seems less probable.

The organotin compounds, the reaction of which with iron pentacarbonyl was investigated in this work, can be divided into three classes. In the first class all the organo-groups are bonded to tin *via* sp^3-hybridized carbon atoms, in the second class both sp^3 and sp^2-hybridized carbon atoms are bonded to tin, while in the third class of organotin compounds only sp^2-hybridized carbon atoms are bonded to tin. In order for a tetraorgano–tin compound to give appreciable yields of a dialkyltin iron tetracarbonyl when heated with iron pentacarbonyl, it is necessary that it belong to class II above. Dimethyldiperfluorovinyltin is an exception, since it did not give dimethyltin iron tetracarbonyl. However, the chemistry of a perfluorovinyl group bonded to tin is somewhat different from that of a vinyl group. Furthermore, the dimethyl derivative was the only dialkyldiperfluorovinyltin compound treated with iron pentacarbonyl. For these reasons no special significance should be attached to the fact that dimethyldiperfluorovinyltin failed to give the expected compound.

A possible mechanism which would account for the fact that groups bonded to tin through sp^2-hybridized carbon atoms are easily removed by iron carbonyl is one in which the initial step involves formation of an unstable complex between the π-orbitals of the vinyl or phenyl groups and the iron atom.

The three dimeric dialkyltin iron tetracarbonyl compounds reported here are pale yellow crystalline solids which afford yellow solutions in diethyl ether, dichloromethane or isohexane. These solutions undergo extensive decomposition in air after a few hours. The solid compounds themselves are partially decomposed after standing in air for a few days. The partially decomposed compounds are brown and are no longer completely soluble in organic solvents. The pure dialkyltin iron tetracarbonyl compounds can be handled for brief periods in air. However, when prepared from dialkyldiphenyltin compounds and iron carbonyl, the crude products are pyrophoric even after all of the iron metal has been removed. For this reason all manipulations, including crystallizations, must be done under nitrogen.

The melting points of the dialkyltin iron tetracarbonyl compounds decrease with increasing molecular weight: $[(CH_3)_2SnFe(CO)_4]_2$ decomposes above 220°; $[(C_2H_5)_2SnFe(CO)_4]_2$ m.p. 184–185.5°; $[(C_4H_9)_2SnFe(CO)_4]_2$ m.p. 110–112°. In this connection it is interesting that from a reaction between iron carbonyl and dibenzyldivinyltin a yellow oil was obtained. This oil was probably crude dibenzyltin iron tetracarbonyl but it could not be purified. The infrared spectrum of each of the compounds in chloroform solution shows three carbonyl bands. These bands are at 2050, 2020, 1985 cm.$^{-1}$ for the butyl compound, at 2050, 2015, 1985 cm.$^{-1}$ for the ethyl compound, and at 2050, 2010, 1980 cm.$^{-1}$ for the methyl compound.

[CONTRIBUTION NO. 538 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

The Chemistry of Sulfur Tetrafluoride.[1] IV. Fluorination of Inorganic Oxides and Sulfides

BY A. L. OPPEGARD, W. C. SMITH, E. L. MUETTERTIES AND V. A. ENGELHARDT

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Sulfur tetrafluoride has been found to be a versatile, easily handled fluorinating agent useful in the preparation of a wide range of inorganic fluorides by replacement of oxygen or sulfur in inorganic compounds. Examples of fluorides prepared from oxides and SF_4 are UF_6, WF_6, IF_5, SeF_4 and GeF_4. Such difficultly obtainable fluorides as SnF_4 and MoF_4 were obtained from the sulfides. The association of SF_4 with certain metal fluorides to form complexes also has been investigated.

Introduction

Sulfur tetrafluoride, a relatively new chemical, has been found to react with most inorganic oxides and sulfides. This general reaction is characterized by replacement of the oxygen or sulfur to give the corresponding fluorides or in some cases the corresponding oxyfluorides, *e.g.*

$$5SF_4 + I_2O_5 \longrightarrow 5SOF_2 + 2IF_5$$

$$6SF_4 + P_4O_{10} \longrightarrow 6SOF_2 + 4POF_3$$

$$SF_4 + SnS_2 \longrightarrow 3S + SnF_4$$

An exception to these class reactions is the oxidation of SF_4 to SF_6 and SOF_4 by strong oxidizing agents such as NO_2 and CrO_3 which will be described in Paper No. V.

In contrast to the reactions of SF_4 with sulfides, the reaction with oxides generally does not consume all of the fluorine bonded to sulfur, and therefore the sulfide fluorination would appear at first glance to be a superior reaction. However, because a number of elements do not form sulfides in the higher oxidation states, such fluorides as WF_6 and IF_5 cannot be obtained by a sulfide fluorination. The merits of the sulfide fluorination reside in the complete utilization of the fluorine atoms in SF_4 and the observed fact that fluorination of sulfides does not stop short of complete replacement as it does in the case of some oxides, *e.g.*

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[1] Paper III, William C. Smith, Charles W. Tullock, Ronald D. Smith and Vaughan A. Engelhardt, THIS JOURNAL, **82**, 551 (1960).

TABLE I

PREPARATION OF IONIC FLUORIDES

Starting mater., *M*	React.,[a] temp., C.	Time, hr.	Prod.	M, % Calcd.	M, % Found	F, % Calcd.	F, % Found	X-Ray
ZnS (0.4) SF_4 (0.2)	60	1	ZnF_2[b]	63.24	62.29 62.50	36.75	33.00 33.33	ZnF_2[c]
HgO (0.1) SF_4 (0.4)	150	10	HgF_2					HgF_2
Bi_2O_3 (0.1) SF_4 (0.6)	100–300	12	BiF_3	78.57	78.77 79.05	21.43	20.67	
FeS_2 (0.2) SF_4 (0.4)	350	6	FeF_3[b]					FeF_3

[a] Reaction carried out in 145-ml. "Hastelloy-C" lined bomb at autogenous pressure. [b] Extracted with CS_2 to remove sulfur. [c] Also contains traces of ZnS.

$$P_4O_{10} + 6SF_4 \longrightarrow 4POF_3 + 6SOF_2$$
$$P_4S_{10} + 5SF_4 \longrightarrow 4PF_5 + 15S$$

The versatility of SF_4 as a fluorinating agent is shown by the preparation of such difficulty obtainable fluorides as IF_5, SeF_4, SnF_4, MoF_6 and UF_6 in high yield by fluorination of I_2O_5, SeO_2, SnS_2, MoO_3 and UO_3 with SF_4 at 250–350° in pressure vessels. The results of the fluorination of oxides and sulfides are summarized.

Ionic Fluorides.—Several different types of ionic fluorides have been obtained by fluorination with SF_4. Zinc sulfide was converted nearly quantitatively to ZnF_2 at 60°. Similarly, Bi_2O_3 at 300° was converted quantitatively to BiF_3. Pyrites (FeS_2) appeared to react completely with SF_4 at 350° to give a product containing FeF_3 as shown by X-ray diffraction. Mercuric oxide was incompletely fluorinated at 150° but X-ray analysis showed the presence of a mercury(II) fluoride phase in the solid product. The reaction conditions are summarized in Table I.

Covalent Fluorides.—A wide range of covalent fluorides and oxyfluorides have been prepared using SF_4 as a fluorinating agent under similar conditions as outlined in Table II. The reaction went especially well with MoO_3 and WO_3 which were converted completely to the volatile hexafluorides at 350°. The reaction of WO_3 with SF_4 in the presence of sodium fluoride gave a white, crystalline solid that was tentatively identified as an impure sample of the Na_2WF_8 described by Cox.[2] Uranium hexafluoride was obtained in 70–80% yields from SF_4 and UO_3, UO_2F_2 and Na_2UO_4 at 100–400°. When U_3O_8 was used UF_4 also was formed.

Molybdenum tetrafluoride was prepared by the reaction of MoS_2 with SF_4 at 350°. The crude product may be extracted with CS_2 to remove the sulfur. Identification of the fluoride was made by simple extraction of the fluoride at room temperature with an ether such as tetrahydrofuran or dimethoxyethane and precipitation of an addition compound by the addition of excess dimethylformamide or dimethyl sulfoxide to the extract.[3] This characterization technique also was applied to the fluorides of TiF_4 and SnF_4 which were obtained in good yields by fluorination of TiO_2 and SnS_2, respectively, at 150–300°.

The reaction of I_2O_5 with SF_4 proceeded smoothly at 150° to give a 70% yield of IF_5. The preparation of SF_4 from sulfur and IF_5 is an oxidation–reduction reaction[4] whereas the preparation of IF_5 using SF_4 is a simple exchange of oxygen and fluorine.

Several fluorides of phosphorus and arsenic were prepared by reaction of the oxides or sulfides with SF_4. Thus, P_4O_{10} reacted rapidly at 150° with SF_4 to yield POF_3, but there was little tendency to form PF_5 even at 250°. Phosphorus pentafluoride was obtained in high yield, however, from the reaction of P_4S_{10} and SF_4 at 300°. Phosphorus thiofluoride was not detected as a product.

SF_4 Complexes.—In some cases, the fluorination products contained large amounts of sulfur tetrafluoride. Such products were obtained only where the metal fluoride is a relatively strong Lewis acid or fluoride ion acceptor. Thus, the product from the GeO_2 fluorination analyzed for $GeF_4 \cdot 2SF_4$. In confirmation of the results of Bartlett and Robinson,[5] BF_3, formed in the B_2O_3–SF_4 reaction, combined with excess SF_4 to form the crystalline $BF_3 \cdot SF_4$. Experiments with SF_4 and covalent fluorides showed definite interaction or compound formation in the systems: HF–SF_4, SbF_5–SF_4, PF_5–SF_4 and AsF_3–SF_4.

The structures of these adducts are not known. Robinson and Bartlett[5] have suggested that they are acid-base complexes, *e.g.*, $F_3B \leftarrow :SF_4$. This formulation does not appear reasonable since SF_4 is a relatively weak donor molecule. Furthermore, the F^{19} magnetic resonance spectrum of the AsF_3–SF_4 system down to −60° shows only one type of fluorine environment because of a rapid exchange of fluorine atoms ($k \geqq 10^3$ sec.$^{-1}$). Association and dissociation of a simple acid-base adduct would not provide a mechanism for exchange of fluorine atoms bonded to arsenic and of those bonded to sulfur.

The adducts may be salts based on the cation SF_3^+. This hypothesis is consistent with the observation that all the fluorides that form adducts are strong fluoride ion acceptors and form stable fluoro anions, *e.g.*, PF_6^-, SbF_6^- and $GeF_6^{=}$. However, mixtures of SF_4 with SiF_4 or IF_5 showed no evidence of complex formation or fast fluorine exchange within the temperature range −90 to 100°.

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(2) B. Cox, B. W. A. Sharp and A. G. Sharpe, *J. Chem. Soc.*, 1242 (1956).

(3) E. L. Muetterties, THIS JOURNAL, **82**, 1082 (1960).

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

(5) N. Bartlett and P. L. Robinson, *Chem. & Ind. (London)*, 1351 (1956).

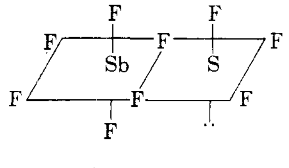
TABLE II: PREPARATION OF COVALENT FLUORIDES[a]

Starting mater., *M*	SF_4, mole	*T.*, °C.	Time, hr.	Product	Analyses % Metal Calcd.	% Metal Found	% F Calcd.	% F Found	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found	Other
B_2O_3 (0.29)	0.8	87–179	1	$SF_4 \cdot BF_3$	18.20[b]	18.62[b]	75.65	75.53							
TiO_2 (0.25)	.75	300	10	$TiF_4 \cdot 2HCON(CH_3)_2$	17.77	17.47	28.17	27.48	26.67	27.84	5.19	5.47	10.38	10.41, 10.46	
GeO_2 (0.075)	.6	100–300	14	$GeF_4 \cdot 2SF_4$	17.75[b]	18.51[b]	62.53	64.12							
SnS_2 (0.2)	.2	300	18	$SnF_4 \cdot 2HCON(CH_3)_2$	34.84	34.35	22.31	21.50	21.13	21.43	4.11	4.06	8.22	8.27	
P_4O_{10} (0.051)	.14	100–250	12	POF_3											Mass spec.
P_4S_{10} (0.025)	.3	200–300	6	PF_5											Mass spec.
SO_2 (0.40)	.5	50–150	8	SOF_2											Mass spec.
SO_3 (0.30)	.6	50–150	8	$S_2O_5F_2$, SO_2F_2, SOF_2											Mass spec.
SeO_2 (0.20)	.8	100–240	14	SeF_4	50.96	51.90	49.04	48.89							
MoS_2 (0.15)	.4	350	8	$MoF_4 \cdot 2(CH_3)_2SO$	29.23	28.81			14.62	14.67	3.69	3.84			
MoO_3 (0.1)	.6	70–350	9	MoF_6											Infrared
WO_3 (0.1)	.6	350	10	WF_6											Infrared
UO_3 (0.1)[c]	.65	100–435	0.5	UF_6											Infrared, m.p. 67–70° (sealed tube)
UO_3 (0.1)	.6	100–200	14	UF_6											Infrared
UO_2F_2 (0.07)[c]	.53	400–425	0.5	UF_6											Infrared
U_3O_8 (0.033)[c]	.37	300–435	0.3	UF_6, UF_4											Infrared, X-ray
I_2O_5 (0.1)	.6	60–150	10	IF_5	57.19	56.15	42.81	44.92							N.m.r.

[a] Reactions run in 145-ml. "Hastelloy-C" lined bomb, autogenous pressure. [b] % Sulfur. [c] Flow system, atmospheric pressure.

Since the fluosilicate anion is a very stable anion, it is difficult to explain the absence of an interaction here. Similarly, IF_5 readily adds F^- to form IF_6^-.

Another type of interaction that is fully consistent with the experimental observations is an association based on fluorine bridge bonds to give a dimeric, *cis*-cyclic or *trans*-linear polymer structure.



This type of interaction is found in HF,[6] SbF_5[7] and $2AsF_3 \cdot 3SO_3$[8] and has been proposed as a fluorine exchange intermediate in SeF_4, SF_4,[9] ClF_3, IF_5[10] and SbF_5.[7] It is notable that most of the fluorides that do interact with SF_4 are not symmetrical molecules. In forming a fluorine bridge complex, these fluorides would attain a higher symmetry, and SF_4 would attain a pseudoöctahedral symmetry.

Experimental[11]

Fluorinations with sulfur tetrafluoride (b.p. −38°) were conducted in glass systems at atmospheric pressure or in pressure vessels. All reactions and transfers of sulfur tetrafluoride and reaction products were carried out in well ventilated hoods and with suitable precautions against personal contact. Sulfur tetrafluoride was prepared from SCl_2 and NaF in refluxing acetonitrile.[4]

The other reagents were of the purest grade available and, when necessary, were dried before using by heating to 150° overnight. Most of the fluorides were prepared in 145-ml. "Hastelloy"-lined bombs under autogenous pressure with agitation. The bomb was charged with the oxide, sulfide or acid, flushed with nitrogen, closed, cooled to −78° and evacuated to 1 mm. After distillation of the desired amount of sulfur tetrafluoride into the bomb, it was closed and heated as specified. After the bomb was allowed to cool to room temperature, volatile materials were vented or transferred *in vacuo* to small (150 ml., 300 ml.) stainless steel cylinders. The procedure then varied depending on the products and the method of characterization.

An alternative method was the use of a flow system at atmospheric pressure. The apparatus was constructed of "Pyrex" glass since only minor etching occurs below 300° if the system is carefully dried and protected from moisture during the reaction. The reaction tube consisted of a "Pyrex" glass tube 1 inch in diameter and 24 inches long. It was fitted at one end with a ground glass closure having a glass inlet tube and thermocouple well. The other end of the tube was expanded into a flask to catch liquid products and a gas outlet tube was provided. The reaction tube was mounted horizontally in a split tube furnace and flexible connections between supply cylinder and product traps were made with "Tygon" plastic tubing. The system was flushed with nitrogen before and after the reaction. Some of the reactions are exothermic and the temperature was controlled by varying the input of heat or SF_4.

The reaction conditions given in the tables may not be optimum since detailed investigations of each system were not made. Since most of the products are well known compounds, no special effort was made to obtain highly purified products and this is reflected in the analytical data. Where

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[6] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 230-231.

[7] C. J. Hoffman, B. E. Holder and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958); E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **79**, 3686 (1957).

[8] E. L. Muetterties and D. D. Coffman, *ibid.*, **80**, 5914 (1958).

[9] E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959).

[10] E. L. Muetterties and W. D. Phillips, *ibid.*, **79**, 322 (1957).

[11] W. C. Smith, U. S. Patents 2,904,394, 2,904,398, 2,904,403, September 15, 1959.

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.

[CONTRIBUTION NO. 539 FROM CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

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

BY WILLIAM C. SMITH AND VAUGHN A. ENGELHARDT

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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).