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Chemistry of Some Sulfur Oxyfluorides[1]

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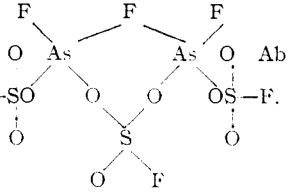
A study has been made of the reactions of sulfur trioxide with inorganic fluorides, mainly those of the Group II and Group VA elements. Fluorosulfonates, $M(SO_3F)_2$, were formed by the alkaline earth fluorides at 200°. The barium and strontium fluorosulfonates pyrolyzed at 500° to give good yields of sulfuryl fluoride whereas the calcium compound reversibly dissociated to calcium fluoride and sulfur trioxide. The very toxic pyrosulfuryl fluoride, $FSO_2–O–O_2SF$, was obtained in good yield when calcium fluoride was treated with a large excess of sulfur trioxide. Arsenic trifluoride and sulfur trioxide exothermally formed $2AsF_3 \cdot 3SO_3$ at room temperature. A structure for this reactive and volatile fluoride, consistent with n.m.r. data, is  Above 30°, there is exchange ($k \sim 10^3$) of the fluorine atoms bonded to arsenic. This exchange may proceed by a rapid process of forming and breaking of the fluorine bridge bonds.

Introduction

There are a number of routes by which inorganic fluorosulfonates can be synthesized. Fluorosulfonic acid, the parent member of this potentially large class of ionic and covalent compounds, has been used for the synthesis of a variety of fluorosulfonates,[2–5] however, the acid is not operable as a starting material in the preparation of some fluorosulfonates. Furthermore, the low volatility of the acid complicates the purification of non-volatile, hydrolyzable fluorosulfonates prepared from the acid. The direct reaction of fluorides with sulfur trioxide which has been used to prepare ionic[6–8] and covalent fluorosulfonates,[9–12] *e.g.*, NH_4SO_3F[6] and $WF_4(SO_3F)_2$[9] appears to be a better general method for fluorosulfonate synthesis because of the high volatility and reactivity of sulfur trioxide. We have explored this method with particular emphasis on the fluorides of Group II and VA elements and have examined some of the chemistry of the products of these reactions.

Discussion

Calcium, strontium and barium fluorides reacted slowly but nearly quantitatively at 200° with 2 moles of sulfur trioxide to form reactive solids. Although no rigorous structural analysis of these solids was made, their properties strongly suggest that they are true fluorosulfonates and not merely lattice compounds. The powder X-ray patterns were unique, and these solids dissolved in water to give solutions that contained the fluorosulfonate ion as indicated by the precipitation of nitron fluorosulfonate, $C_{20}H_{16}N_4 \cdot HSO_3F$, on the addition of nitron acetate to the solutions.

In confirmation of literature reports,[3] the fluorosulfonates of strontium and barium pyrolyzed to the corresponding sulfates and sulfuryl fluoride

$$M(SO_3F)_2 \longrightarrow MSO_4 + SO_2F_2$$

Conversions of about 50% to sulfuryl fluoride were realized by heating the fluorosulfonates *in vacuo* for 3 hr. at 500°. The yields were nearly quantitative. Calcium fluorosulfonate, however, gave only trace to 4% conversions to sulfuryl fluoride. The pyrolysis was characterized as a nearly quantitative, reversible dissociation to starting materials

$$Ca(SO_3F)_2 \rightleftarrows CaF_2 + 2SO_3$$

The differences in the pyrolysis behavior of the alkaline earth fluorosulfonates may reflect slight variations in the solid state structures. For example, the coördination number may be six for calcium ion and eight for strontium and barium. Such variations coupled with the decrease in cation polarizing power in going from calcium to barium might lead to different mechanisms for the breakdown of the fluorosulfonate lattices. Potassium fluorosulfonate yields sulfur trioxide not sulfuryl fluoride on thermal decomposition whereas sodium fluorosulfonate pyrolyzes in a manner that appears to be formally similar to that of the calcium salt to give sodium fluoride and sulfur trioxide as well as sodium sulfate and sulfuryl fluoride.[13] On the other hand, the differences in pyrolysis behavior may have a thermodynamic basis. An attempt was made to verify this possibility by treating sulfuryl fluoride and calcium sulfate but without success. This reaction was attempted at 500°, and, in view of the "inert" character[14] of sulfuryl fluoride, it is quite possible that equilibrium conditions were not achieved.

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[1] Presented before the Division of Inorganic Chemistry, National Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

[2] W. Traube, *Ber.*, **46**, 2525 (1913).

[3] W. Traube, J. Hoerenz and F. Wunderlich, *ibid.*, **52**, 1272 (1919).

[4] M. Trautz and K. Ehrmann, *J. prakt. Chem.*, **142**, 79 (1935).

[5] E. Hayek, J. Puschmann and A. Czaloun, *Monatsh. Chem.*, **85**, 359 (1954).

[6] W. Traube, *Ber.*, **46**, 2513 (1913).

[7] H. A. Lehmann and L. Kolditz, *Z. anorg. allgem. Chem.*, **272**, 69 (1956).

[8] E. Hayek, A. Czaloun and B. Krismer, *Monatsh. Chem.*, **87**, 741 (1956).

[9] H. C. Clark and H. J. Emeleus, *J. Chem. Soc.*, 4778 (1957).

[10] H. C. Clark and H. J. Emeleus, *ibid.*, 190 (1958).

[11] E. L. Muetterties, U. S. Patent 2,832,667 (April 29, 1958).

[12] A. Engelbrecht, A. Aignesberger and E. Hayek, *Monatsh. Chem.*, **86**, 470 (1955).

[13] Reference 7, footnote 10.

[14] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 94.

Magnesium and beryllium fluorides seemed to differ in degree from the other alkaline earth fluorides in their reactions with sulfur trioxide. At 200°, the reactions were very slow, and the products had empirical compositions of the order $MF_2 \cdot (0.3\text{–}0.4)SO_3$. Like calcium fluorosulfonate, these magnesium and beryllium compounds pyrolyzed to sulfur trioxide and the respective fluorides; only trace amounts of sulfuryl fluoride were formed. Mercuric fluoride, a Group IIB fluoride, reacted with sulfur trioxide at 500° to give sulfuryl fluoride in 25% conversion. Zinc fluoride formed a fluorosulfonate at 200° and this compound decomposed at 500° to give mainly sulfuryl fluoride.

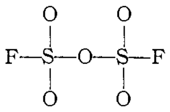
Pyrosulfuryl fluoride was formed when calcium fluoride reacted at 100–300° with excess sulfur trioxide and then was treated with 60–98% sulfuric acid at 25°.[15]

$$CaF_2 + 3SO_3 \longrightarrow CaSO_4 + FSO_2OSO_2F$$

The yields, based on CaF_2, varied from 0 to 16 to 72% for mole ratios (SO_3 to CaF_2) of 2:1 to 4:1 to 9:1. The sulfuric acid treatment was necessary for good yields in this reaction. The sulfuric acid step suggests that an intermediate in this process may be $Ca(S_2O_6F)_2$[16] and a *speculative* sequence is

$$CaF_2 \xrightarrow{SO_3} Ca(SO_3F)_2 \xrightarrow{SO_3}$$
$$Ca(S_2O_6F)_2 \xrightarrow{H_2O\ (\text{ex. } H_3SO_4)} CaSO_4 + H_2SO_4 + S_2O_5F_2$$

Pyrosulfuryl fluoride is an unusual compound. The structure has not been established rigorously but the infrared spectrum[10] and F^{19} magnetic resonance spectrum are consistent with the structure



$$F-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{S}}-O-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{S}}-F$$

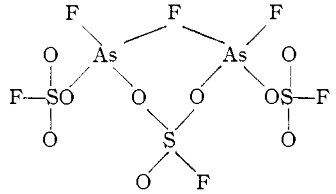
This fluoride has an inhalation toxicity of the same order as that of phosgene (lethal to rats at 10 p.p.m. in a four-hour exposure period) and a thermal stability unique for a compound that has a sulfur–oxygen–sulfur linkage. Thermal decomposition to sulfuryl fluoride does not occur at a measurable rate below 200° but it is fast at 500°.

$$S_2O_5F_2 \longrightarrow SO_2F_2 + SO_3$$

Above 500° increasing amounts of thionyl fluoride are formed; the ratio of SO_2F_2:SOF_2 was 9:1 at 676°. Thionyl fluoride may have been formed here in a secondary reaction consisting of the pyrolysis of sulfuryl fluoride; pyrolysis of sulfuryl fluoride to thionyl fluoride above 500° was established in independent experiments. Conversion of pyrosulfuryl fluoride to sulfuryl and thionyl fluoride was also effected by chemical reduction with such agents as sulfur and carbon monoxide.

The Group VA trifluorides differed in type as well as in degree in their reactions with sulfur trioxide. Nitrogen trifluoride was inert to sulfur trioxide at temperatures below 100°. Phosphorus trifluoride was absorbed by sulfur trioxide to form what appeared to be a weak complex: $F_3P \rightarrow SO_3$; temperatures up to 200° were insufficient to effect reaction to give a fluorosulfonate or a sulfur oxyfluoride. Antimony trifluoride formed a solid that appeared to be mainly the tris-fluorosulfonate, $Sb(SO_3F)_3$. This compound was non-volatile and thermally decomposed reversibly to sulfur trioxide and the trifluoride (very small amounts of pyrosulfuryl fluoride were detected). Arsenic trifluoride reacted exothermally at room temperature with sulfur trioxide to form a volatile compound that analyzed for $2AsF_3 \cdot 3SO_3$.[11]

Engelbrecht, Aignesberger and Hayek[12] and coworkers have suggested that $2AsF_3 \cdot 3SO_3$ is not a fluorosulfonate but an acid–base complex of some type. However, the F^{19} magnetic resonance spectrum of the compound was found to consist of three peaks of relative intensity 3:2:1. The peak of intensity three was in the region characteristic of fluorine bonded to sulfur; the other two peaks were in the region of the AsF_3 resonance. A structure consistent with these data and with the rather high volatility (b.p. 141.9° (760 mm.)) for a compound of this molecular weight is



When this compound is heated above 30°, the two peaks of the F^{19} spectrum ascribed to the terminal and to the bridge fluorine atoms attached to arsenic broaden and finally merge. This is indicative of fluorine exchange[17] (fluorine atoms bonded to arsenic), and exchange could proceed readily by a rapid process of forming and breaking of bridge bonds.

Arsenic fluorosulfonate proved to be a relatively strong sulfonating and fluorinating agent. Benzene was converted at 0° to a mixture of benzenesulfonic acid and diphenyl sulfone. Carbon tetrachloride underwent a rather complex fluorination and oxidation, and the products ranged from chlorofluoromethanes to carbonyl fluoride and carbonyl chlorofluoride. Arsenic fluorosulfonate did not decompose irreversibly at 500°; only trace amounts of sulfuryl fluoride were formed at these temperatures.

Experimental

Reagents.—Baker and Adamson "Sulfan B" sulfur trioxide was used directly without purification. Commercial samples of the Group II fluorides after drying *in vacuo* at 100–250° totaled at least 98% metal and fluorine. Arsenic trifluoride was prepared from arsenic (III) oxide, calcium fluoride and sulfuric acid.[18] The crude product was stored over sodium fluoride pellets and was distilled prior to use. Commercial samples of antimony trifluoride were purified by sublimation. Phosphorus trifluoride was prepared from the trichloride and antimony trifluoride ($SbCl_5$ catalyst).[19]

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(15) E. L. Muetterties, U. S. Patent 2,801,904 (August 6, 1957).

(16) The compound KS_2O_6F has been prepared from KF and SO_3. Lehmann and Kolditz, ref. 7.

(17) Exchange phenomena of sufficiently high frequency have been shown capable of collapsing a two-line spectrum into a single, concentration-dependent resonance; H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(18) "Inorganic Syntheses," Vol. IV, McGraw–Hill Book Co., Inc., New York, N. Y., 1953, p. 150.

(19) H. S. Booth and F. C. Mericola, THIS JOURNAL, **62**, 640 (1940).

The commercial sample of nitrogen trifluoride was found to be optically (infrared and mass spectrographic) pure. Sulfuryl fluoride, prepared by reaction of sulfur dioxide and silver (II) fluoride,[20] was purified by distillation. Pyrosulfuryl fluoride was also prepared by the bomb tube reaction of IF_5 (432 g.) and SO_3 (160 g.) at 100°; purification was effected by treatment with sulfuric acid and distillation.[21]

Synthesis of the Alkaline Earth Fluorosulfonates.—A "Hastelloy C"-lined vessel of 115 ml. internal capacity was charged with 0.5 mole of alkaline earth fluoride and 1.0 mole of sulfur trioxide. The vessel was cooled to about $-78°$ and then evacuated to <1 mm. The reaction system was heated to 200° for a period of 12 to 96 hours (a 12–24 hour period proved to be sufficient for complete reaction of calcium, strontium and barium fluorides). At the completion of the reaction period, the gaseous materials, if any, were bled from the hot (100–200°) vessel. Traces of gaseous materials were removed by evacuation of the vessel to <1 mm. The solid products, which were 92–99% soluble in water (complete conversion to fluorosulfonates would be indicated by 100% water solubility[6]) and whose solutions gave precipitates of nitron fluorosulfonate[22] on addition of nitron acetate, analyzed for $M(SO_3F)_2$. In confirmation of literature[23] reports, the fluorosulfonates were too readily hydrolyzed by water to permit purification with this solvent.

Anal. Calcd. for $Ca(SO_3F)_2$: Ca, 16.79; F, 15.95; S, 26.88 Found: Ca, 17.04, 16.87, 17.21; F, 15.88, 15.67, 16.03; S, 26.02, 26.56, 27.00. Calcd. for $Sr(SO_3F)_2$: Sr, 30.66; F, 13.30; S, 22.40. Found: Sr, 31.01; F, 13.05; S, 21.14. Calcd. for $Ba(SO_3F)_2$: Ba, 40.94; F, 11.33; S, 19.08. Found: Ba, 42.54; F, 10.83; S, 18.81.

The X-ray powder patterns of these compounds were unique and either did not show the lines of the starting materials or showed only very weak lines characteristic of the starting materials. The compounds if ground in a mortar before X-ray analysis inexplicably showed the lines of the respective sulfates. Apparently, there was sufficient moisture present in the "dry box," used for handling these compounds, to hydrolyze them during the grinding process. When the solids were put directly into capillaries, unique powder patterns were obtained. The fluorosulfonates should be isomorphous with the corresponding perchlorates but no literature data on the X-ray patterns for the anhydrous alkaline earth perchlorates were found.[24]

Beryllium and magnesium fluorides appeared to react with sulfur trioxide only to a minor degree under the conditions described above. Typical analyses for products obtained in 24-hour reaction periods are listed below.

Anal. Calcd. for $Be(SO_3F)_2$: Be, 4.36; F, 18.35; S, 30.96. Found: Be, 13.68; F, 51.27; S, 8.72. Calcd. for $Mg(SO_3F)_2$: Mg, 10.94; F, 17.09; S, 28.83. Found: Mg, 28.46; F, 34.74; S, 12.14.

Pyrolysis of Fluorosulfonates.—Pyrolyses of the barium and strontium fluorosulfonates and the beryllium fluoride– and strontium fluoride–sulfur trioxide products were effected in the previously described pressure vessel. Twenty-five to thirty-gram samples were placed in the vessel which then was connected to a vacuum pump through a trap cooled in liquid nitrogen. The vessel was heated to 500 ± 10° for a period of 3 hr. The gaseous products were roughly fractionated to separate SO_3 from the low-boiling gases and were analyzed by infrared and mass spectrometry. The results are summarized in Table I.

The X-ray powder patterns of residual solids showed mainly the lines of the sulfate in the case of barium and strontium and mainly the lines for the fluorides in the case of magnesium and beryllium.

Calcium fluorosulfonate was pyrolyzed by the procedure described above for the other alkaline earth fluorosulfonates and was also pyrolyzed in a heated nickel tube at temperatures up to 680° *in vacuo* and at atmospheric pressure using a flow of nitrogen gas to sweep out the product. None of these procedures had any significant effect on the distribution of the products. The fluorosulfonate also was prepared in a pressure vessel and then immediately pyrolyzed; this procedure was followed to be certain that inadvertent exposure to atmospheric moisture was not responsible for the low conversion to sulfuryl fluoride. Of some 20 pyrolyses, 19 gave trace to 1% conversions to sulfuryl fluoride and one run, never duplicated, gave a 4% conversion to sulfuryl fluoride. The details from two typical runs and the one "atypical" run are listed below in Table II.

TABLE I

PYROLYSIS OF FLUOROSULFONATES

Fluoride	% Conversions to SO_3	% Conversions to SO_2F_2	% Yield of SO_2F_2
$Ba(SO_3F)_2$	1^a	56	66
$Sr(SO_3F)_2$	1^a	65	90
$MgF_2 \cdot XSO_3$	50	Trace	Trace
$BeF_2 \cdot XSO_3$	47	Trace	Trace

[a] Found mainly as SO_2.

TABLE II

PYROLYSIS OF $Ca(SO_3F)_2$

	Run 1	Run 2	Run 3
Temp., °C.	500	500	500
Time, hr.	2	5	12
% Conver. SO_3	82	94	90
% Conver. SO_2F_2	1	<1	4
Comp. of residual solid			
% Ca	47.96	49.70	48.25
% F	42.06	43.53	43.26
% S	3.19	2.46	1.31
X-ray	CaF_2	CaF_2	CaF_2

Since there was a possibility that CaF_2 and SO_3 may initially form a lattice compound that might pyrolyze to CaF_2 and SO_3 and that this would only slowly convert to $Ca(SO_3F)_2$ at 200°, one preparation of the calcium compound was run for 120 hr., and this product then was pyrolyzed. This is "Run 2" listed in Table II; obviously the longer synthesis time did not affect the course of the pyrolysis. A sample of $Ca(SO_3F)_2$ prepared by the literature procedure[25] from CaF_2 and HSO_3Cl also gave only about 2% yield of SO_2F_2. Use of calcium fluoride that contained small amounts (1–3%) of iron (III) and nickel (II) fluorides in the preparation of $Ca(SO_3F)_2$ gave a product that yielded less than 1% SO_2F_2 on pyrolysis. Addition of 1–5% hydrogen chloride to the pyrolysis system did not affect the distribution of products.

Half molar quantities of calcium sulfate and sulfuryl fluoride were allowed to react in the pressure vessel at 500° for 12 hr. No evidence of reaction was indicated by infrared analysis of the gaseous product and fluorine analysis of the solid product.

Mercury (II) fluoride (0.25 mole) and sulfur trioxide (0.25 mole) were heated in the previously described pressure vessel for a period of 3 hr. at 500°. Infrared analysis of the gaseous product showed it to consist mainly of SO_2F_2 (small amounts of SO_2 were present). The conversion to SO_2F_2, based on HgF_2, was 25%.

Zinc fluoride (0.1 mole) and sulfur trioxide (0.2 mole) were heated in a pressure vessel for a period of 24 hr. The vessel was then evacuated to remove any unreacted sulfur trioxide. The remaining solid product was analyzed, and the low sulfur and high fluorine indicated that formation of $Zn(SO_3F)_2$ was incomplete.

Anal. Calcd. for $Zn(SO_3F)_2$: F, 14.4; S, 24.3. Found: F, 17.62; S, 15.08.

This product decomposed at 500° in a pressure vessel. Roughly half of the sulfur content of the solid was converted to sulfuryl fluoride. Only traces of sulfur oxides were detected in the pyrolysis gases by the mass spectrograph.

Synthesis of Pyrosulfuryl Fluoride.—A stainless steel-lined pressure vessel of 400-ml. internal capacity was charged with 0.5 mole of calcium fluoride and 1.0 to 9.0 moles of sulfur trioxide. The vessel was cooled to about $-78°$ and evacuated to <1 mm. pressure. The reaction mixture was

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(20) H. J. Emeleus and J. P. Wood, *J. Chem. Soc.*, 2183 (1948).

(21) W. Schmidt, *Monatsh. Chem.*, **85**, 452 (1954).

(22) W. Lange has described the fluorosulfonate salt of nitron, an organic base ($C_{20}H_{16}N_4$); *Ber.*, **60**, 962 (1927).

(23) J. H. Simons, ref. 14, p. 173.

(24) J. D. H. Donnay and W. Nowacki, "Crystal Data," The Geological Society of America, Memoir 60, New York, N. Y., 1954.

(25) R. K. Iler, U. S. Patent 2,312,413 (March 2, 1943).

heated to 100–300° under autogenous pressure for periods of 4 to 36 hr. (the vessel was agitated during the heating period) and then cooled to −20 to 0°. Sufficient sulfuric acid of 70 to 98% concentration to convert unreacted SO_3 to H_2SO_4 was then injected into the vessel. The product at this point was a slurry, and the pyrosulfuryl fluoride which is immiscible with sulfuric acid was recovered by decantation, distillation or both (b.p. 50.8° (760 mm.)). A detailed summary of the effects of reaction variables on the conversion of fluorine in CaF_2 to fluorine in $S_2O_5F_2$ is given in Table III. The pyrosulfuryl fluoride was characterized by vapor pressure and vapor density measurements and by infrared analysis. The F^{19} magnetic resonance spectrum of this fluoride consisted of a single peak that fell in a field characteristic of the fluorine resonance in SOF_2 and SO_2F_2.

TABLE III

SYNTHESIS OF $S_2O_5F_2$

SO_3/CaF_2 mole ratio	Temp., °C.	Time, hr.	92% sulfuric acid, g.	% Conversion of CaF_2 to $S_2O_5F_2$
2:1	200	24	288	Trace
4:1	200	24	288	16.5
4:1	200	12	288	7.6
4:1	100	24	182	<1
4:1	150	24	182	8
4:1	300	6	182	1
7:1	200	24	364	45
9:1	200	24	500	72
4:1[a]	200	24	182	25.3
4:1	200	24	None	1–4

[a] BF_3 present in catalytic amounts.

Pyrosulfuryl fluoride was found to be a highly toxic substance by inhalation tests with male albino rats. The vapor of this fluoride was lethal to 2 out of 2 rats at 35 p.p.m. and was lethal to 1 out of 2 rats at 10 p.p.m. (exposure periods of 4 hr.). At the lower concentration, the rat died within 24 hr. after the end of the exposure. During exposure the rats exhibited cyanosis, dyspnea and blinking. The inhalation of 1.6 p.p.m. for 4 hr. was not fatal to 2 rats tested at this concentration. The approximate lethal concentration for a 4-hr. exposure is 10 p.p.m. This fluoride also was established as toxic by oral administration, but the order of toxicity was not established because of solvent dilution problems.

The compound $S_3O_8F_2$ has been described in the literature, and this oxyfluoride was a conceivable product never detected from the CaF_2–SO_3 reaction. A sample of $S_3O_8F_2$ was prepared by the procedure of Lehman and Kolditz,[26] which consists of the treatment of a saturated solution of BF_3 in SO_3 with 70% H_2SO_4. Both $S_2O_5F_2$ and $S_3O_8F_2$ were obtained in about 10% yields; the $S_3O_8F_2$ boiled at 82° (310 mm.). Pyrolysis of $S_3O_8F_2$ in a pressure vessel was complete in 4 hr. at 150°; $S_2O_5F_2$ was the only fluorine-containing product. Therefore, $S_3O_8F_2$ could be a product in the CaF_2–SO_3 reaction, but under the experimental conditions it would be decomposed to $S_2O_5F_2$.

Reduction of Pyrosulfuryl Fluoride.—Pyrolyses and chemical reductions of $S_2O_5F_2$ were effected by two procedures: (1) by heating the fluoride in a Hastelloy C-lined vessel and (2) by passing the fluoride through a heated nickel or platinum tube that was packed with CaF_2 pellets. Products were identified by mass spectrographic or infrared analysis. The details of the pyrolyses and chemical reductions are listed in Table IV.

TABLE IV

PYROLYSIS AND CHEMICAL REDUCTION OF $S_2O_5F_2$

Temp., °C.	Co-reactant	Reactor	Contact time, hr.	Molar ratios of fluorine products
200	.....	Bomb	10	$S_2O_5F_2$[a]
500	.....	Bomb	3	$3S_2O_5F_2:7SO_2F_2$
588	.....	Tube	1/6	SO_2F_2[b]
676	.....	Tube	1/3	$9SO_2F_2:SOF_2$
400	S or CO	Bomb	3	SO_2F_2[b]
600	CO	Tube	1/10	$SO_2F_2:SOF_2$

[a] Trace of SO_2F_2. [b] Trace of SOF_2.

Sulfuryl fluoride was subjected to comparable pyrolysis conditions. Pyrolysis of SO_2F_2 was relatively slow at temperatures of 700–1000° with contact times of 5–30 minutes. The molar ratio of SO_2F_2 to SOF_2 in the product was 19:1 and 8.1:1 at 890 and 1080°, respectively.

Reactions of SO_3 and Group V Trifluorides.—Roughly equimolar amounts of nitrogen trifluoride and sulfur trioxide (total pressure 200 mm.) were heated in a closed 100-ml. glass vessel to 100°. There was no evidence of reaction in a period of 0.5 hr.

Phosphorus trifluoride showed a high solubility in sulfur trioxide. Distillation of a saturated solution gave only the starting materials. The F^{19} magnetic resonance spectrum of a saturated solution showed only the characteristic doublet (J/γ M = 621 c.p.s.) of PF_3. Therefore, any reaction of PF_3 and SO_3 at 20–30° must be limited to a weak donor–acceptor interaction and this complex, $F_3P{\cdot}SO_3$, must be highly dissociated at room temperature. There was no evidence of reaction between SO_3 and PF_3 when these were heated in a pressure vessel to 200°; no fluorosulfonates or sulfur oxyfluorides were detected spectroscopically in the reaction mixture.

Arsenic trifluoride reacted exothermally with sulfur trioxide at room temperature. The reaction was carried out in a two-necked flask fitted with a water-cooled reflux condenser and a dropping funnel. Two addition procedures, AsF_3 to SO_3 and SO_3 to AsF_3, were used. The arsenic–fluorine product of the reaction was the same no matter what the molar ratio of reactants or the order of addition; however, when excess sulfur trioxide was employed, small amounts of $S_2O_5F_2$ were formed. The arsenic product boiled at 141.9° (760 mm.) and analyzed for $2AsF_3{\cdot}3SO_3$. The yields were nearly quantitative.

Anal. Calcd. for $2AsF_3{\cdot}3SO_3$: As, 29.73; F, 22.62 S, 19.08. Found: As, 29.02, 30.49; F, 20.61, 23.56; S, 20.59, 19.19.

The F^{19} magnetic resonance spectrum consisted of three peaks of relative intensities 3:2:1. The peak of relative intensity 3 was in a region characteristic of S–F bonds in fluorosulfonates and sulfur oxyfluorides, and the other two peaks were in the region characteristic of the As–F bond. When the sample was heated, the peaks of relative intensities 1 and 2 began to broaden and ultimately merged, but the third peak was temperature insensitive. At ~ 50°, the average lifetime of fluorine atoms (bonded to arsenic) in a given environment is $\tau \cong {}^1/_4\,\delta\,\omega \cong 10^{-3}$ sec. Mass spectrographic analysis of the fluorosulfonate showed only the mass numbers characteristics of AsF_3 and SO_3, indicating a reversible decomposition of the fluorosulfonate.

Antimony trifluoride (90 g.) and sulfur trioxide (106 g.) reacted in a Hastelloy C-lined vessel at 120° for 8 hr. A fuming solid (211 g.) was the product and this was heated *in vacuo* at 50°. In this manner 10 g. of $S_2O_5F_2$ and 10 g. of SO_3 were volatilized and recovered. The solid residue was not a pure compound and could not be purified by distillation or crystallization. The analysis suggested that the major phase in the solid was $Sb(SO_3F)_3$.[27]

Anal. Calcd. for $Sb(SO_3F)_3$: Sb, 29.08; F, 13.61; S, 20.57. Found: Sb, 28.83; F, 10.00; S, 22.38.

This solid pyrolyzed at 150–200° *in vacuo* to yield sulfur trioxide as the only volatile product. No sulfur oxyfluorides were detected by infrared and mass spectrographic analysis of the product.

Chemistry of Arsenic Fluorosulfonate.—Arsenic fluorosulfonate (10 g.) was added slowly to benzene (25 g.). The reaction was highly exothermic, and the benzene was cooled externally with ice. The resultant product was shown by infrared analysis to contain benzenesulfonic acid and diphenyl sulfone. The latter was isolated and analyzed.

Anal. Calcd. for $(C_6H_5)_2SO_2$: C, 66.02; S, 14.69; H, 4.62. Found: C, 66.17; S, 14.57; H, 4.61.

At 20°, arsenic fluorosulfonate reacted violently with *n*-butyl chloride, slowly with cyclohexene and not detectibly with chloroform and carbon disulfide. Carbon tetrachloride

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(26) H. A. Lehman and L. Kolditz, *Z. anorg. allgem. Chem.*, **272**, 73 (1953).

(27) E. Hayek, A. Czaloun and B. Krismer, ref. 8, found that electrolysis of $AgSO_3F$ in acetonitrile with antimony electrodes led to the formation of $Sb(SO_3F)_3{\cdot}2CH_3CN$. The acetonitrile could not be removed from the complex fluorosulfonate without secondary decomposition taking place.

underwent a complex reaction with the fluorosulfonate at 200–350° in a pressure vessel. At 200°, 40 g. of arsenic fluorosulfonate and 30 g. gave a gas which infrared analysis showed to contain COFCl, CF_2Cl_2, SO_2, COF_2, $COCl_2$ and SO_2F_2 in the approximate molar ratios of 8:8:1:1:1:trace, respectively. At 300° the amounts of SO_2, SO_2F_2 and COF_2 increased, and significant quantities of CF_3Cl were formed.

Arsenic fluorosulfonate was vaporized in a stream of nitrogen through a nickel tube heated to 500°. The condensate in the liquid nitrogen trap contained trace amounts of SO_2F_2 and SO_2; the remainder of the condensate consisted solely of arsenic fluorosulfonate. This experiment and the mass spectrographic data point to a reversible decomposition of the fluorosulfonate.

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[CONTRIBUTION FROM THE IDAHO STATE COLLEGE]

Adsorption of Fluoride from Dilute Aqueous Solution. Adsorption by Synthetic Zirconyl Silicate and Other Materials

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Some studies on the fluoride adsorbancy of synthetic calcium monohydrogen phosphate and synthetic sintered and unsintered zirconium silicate and beryllium silicate were made. Ten p.p.m. of fluoride was passed at about 0.3 ml./min. through chromatographic tubes packed with the material under study together with diatomaceous earth, and the concentration of the fluoride in the effluent solution determined. The materials which were sintered with glass adsorbed very slight amounts of fluoride. Calcium phosphate and unsintered beryllium silicate adsorbed about half of the fluoride from 50 ml. of 10 p.p.m. fluoride solution. Unsintered zirconium silicate adsorbed all detectable fluoride from such a solution. One gram of zirconium silicate adsorbed as much as 5 mg. of fluoride from solution. Passing 0.1 *N* sodium carbonate through the zirconium silicate columns caused adsorbed fluoride to be released; however, the extent of fluoride recovery by this method varied unpredictably between 30 and 100%.

This paper is a report on a study of fluoride adsorption by certain selected materials. The enamel and dentine of teeth, bone and hydroxylapatite are known to adsorb fluoride[1] as is glass.[2] R. C. Specht[2] showed that borosilicate glass and soft glass could adsorb fluoride and release it quantitatively upon treatment with ferric sulfate solution and sodium hydroxide solution. He packed finely ground glass into glass tubing through which he passed the fluoride and subsequently the ferric sulfate and sodium hydroxide solutions. A similar approach was used for this study.

The materials investigated included a calcium phosphate prepared by adding phosphoric acid to a suspension of calcium carbonate and sintered and unsintered beryllium and zirconyl silicates precipitated from water glass. X-Ray diffraction indicates that the calcium phosphate is principally calcium monohydrogen phosphate. Calcium phosphate was selected since it is a major constituent of the enamel of teeth. Both beryllium and zirconium in solution are strongly attracted to fluoride ions,[3] hence their silicates might adsorb fluoride. The silicates were chosen because of their insolubility and since glass, a silicate, is a fluoride adsorber. The zirconium and beryllium silicates were sintered with glass in an effort to modify their surfaces and their fluoride adsorbing ability. Preliminary studies (see Table I) showed that only the unsintered zirconium silicate completely removed the fluoride from a 10 p.p.m. fluoride solution passed through it.

Apparatus and Procedure.—The apparatus consisted of chromatographic tubes packed with the material under investigation with glass–Teflon needle valves (Emil Greiner Co., N. Y. C.) attached to the top of the tubes and connected by rubber tubing to Marriotte bottles which contained the solutions to be passed through the columns. The needle valves were connected at the top of the tubes to lessen the chance of their becoming clogged. The most convenient tube was a 400 × 20 mm. one piece unit fitted with a coarse fritted disc. The glass–Teflon needle valve was the most controllable of the valves tried at the 0.3 ml./min. rate of flow used.

The chromatographic tubes were packed as follows. One gram of diatomaceous earth was made into a slurry which was poured into the bottom of the tube to protect the fritted disc from the active materials; then another slurry containing about two grams of the active material mixed with about two grams of diatomaceous earth was poured into the tube and followed by a third slurry of 2 g. of diatomaceous earth to protect the active layer when solutions above the packing material were changed. After this pad had formed, the excess water above which contained the fine slow settling particles was poured off, and the column was refilled with water and washed for about 5 hours at 1.5 ml./min. Then the water flow was stopped, the water poured off and 10 p.p.m. of fluoride solution added to the column and allowed to flow at about 0.3 ml./min. Next, in the case of the zirconium silicate columns, the fluoride solution was poured off and 0.1 *N* sodium carbonate passed through the column at about 0.4 ml./min. Sodium carbonate was used for removal of fluoride since sodium hydroxide appeared to react with the zirconium silicate and the fritted disc. A basic solution was used since it is known to attack silicates.

In the case of zirconium silicate, two general procedures for running the columns were employed. In one about 100 ml. of solution containing 10 p.p.m. of fluoride was passed through the column and collected as a single sample; then about 150 ml. of 0.1 *N* sodium carbonate was passed through, collected in two fractions and the fluoride concentrations in these fractions determined. This procedure yielded the more quantitative recovery of fluoride but no information about the total adsorptive ability of the material. In the second procedure about five 100-ml. fractions of effluent from the 10 p.p.m. of fluoride were collected, and then from two to six fractions of about 1000 ml. each were collected. Determinations of fluoride in these fractions were performed while the columns were running to determine the time when the column packing material would not adsorb more fluoride. Actually, for the total volume of fluoride solution run

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(1) J. F. Volker, H. C. Hodge, H. J. Wilson and S. N. Voorhis, *J. Biol. Chem.*, **134**, 534 (1940).

(2) R. C. Specht, *Anal. Chem.*, **28**, 1015 (1956).

(3) F. Feigl, "Specific, Selective and Sensitive Reactions," Academic Press, New York, N. Y., 1949.