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Fluorination of Inorganic Sulfur Compounds[*1]

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Sulfuryl fluoride has been prepared by a number of methods, including the fluorination of sulfur dioxide,[1–7] sulfur trioxide,[8,9] sulfuryl chloride,[2–4,10,11] and sodium sulfate or sodium sulfite[12] by the use of various inorganic fluorinating agents. The thermal decompostion of barium fluorosulfonate has been known to yield sulfuryl fluoride.[13] The formation of sulfuryl fluoride has also been observed in the electrochemical fluorination of fluorosulfonic acid[14] and in that of several inorganic sulfur compounds.[15] In the electrolysis of a liquid mixture of sulfur dioxide and hydrogen fluoride at a low temperature,[16] and in that of inorganic sulfur compounds in fused potassium-dihydrofluoride,[15] sulfuryl fluoride was found among the products.

Sulfuryl fluoride is a useful commercial fluorochemical; it is, for example, a good insecticidal fumigant.[17] In the course of our studies of the electrochemical fluorination of gaseous compounds,[18] we have now found that sulfuryl fluoride can be readily produced in a good yield directly from gaseous sulfur dioxide. This electrochemical process involves the bubbling of the starting material into anhydrous liquid hydrogen fluoride. In the present paper, emphasis will be placed on the application of this recently-developed electrochemical method of the fluorination of gaseous compounds for the production of sulfuryl fluoride.

The electrochemical fluorination of related sulfur compounds, such as thionyl fluoride, thionyl chloride, sulfuryl chloride, sulfur mono-, and dichlorides, was also carried out in order to clarify their behavior in the fluorination.

Experimental

Materials. Sulfur dioxide (99.9%) was obtained from the Takachiho Chemical Industrial Co. Thionyl fluoride was prepared by the procedure given in the literature.[19] Thionyl chloride, sulfuryl chloride, sulfur mono-, and dichlorides were redistilled under atmospheric pressure or at reduced pressure before use. Anhydrous hydrogen fluoride (99%) was used after preliminary electrolysis.

Fluorination of Sulfur Dioxide. The apparatus and procedures for the fluorination have previously been described.[20] The electrolysis was carried out without using a conductivity additive. The exit gases from the sodium fluoride tube were regularly monitored by gas chromatography by taking the sample through a sampling valve placed immediately after the tube. Chromatographic analyses were carried out with a Shimadzu GC-2C model chromatograph, using a 0.3 cm i.d. × 6 m column packed with 60% (by wt) perfluoro-tri-*n*-butylamine[*2] on 60/80 mesh Celite 545 SK.[*3] (Column temperature: 0°C; carrier gas: helium).

The products formed (in the order of their peak appearance in the chromatogram) were as follows:

[*1] "Electrochemical Fluorination of Gases." Part VI.

1) H. Moissan and P. Lebeau, *Compt. rend.*, **132**, 374 (1901).

2) H. J. Emeléus and J. F. Wood, *J. Chem. Soc.*, **1948**, 2183.

3) M. M. Woyski, *J. Am. Chem. Soc.*, **72**, 919 (1950).

4) L. J. Belf, Brit. Pat. 727062 (1955).

5) R. Ruh, R. A. Davis and K. A. Allswede, U. S. Pat. 3092458 (1963).

6) L. G. Anello and C. Woolf, U. S. Pat. 3107979 (1963); Japanese Pat. Publ. 4051 (1963).

7) A. G. Bisignani and R. H. Edgecomb, U. S. Pat. 3320030 (1967).

8) H. A. Pacini and A. E. Pavlath, U. S. Pat. 3132925 (1964).

9) J. R. Soulen, U. S. Pat. 3146068 (1964).

10) K. Wiechert, *Z. anorg. allgem. Chem.*, **261**, 310 (1950).

11) W. Sundermeyer, *ibid.*, **314**, 100 (1962).

12) M. Picon and L. Domange, *Compt. rend.*, **236**, 704 (1953).

13) W. Traube, J. Hoerenz and F. Wunderlich, *Ber.*, **52**, 1272 (1919).

14) H. Schmidt and H. D. Schmidt, *Z. anorg. allgem. Chem.*, **279**, 289 (1955).

15) A. Engelbrecht, E. Mayer and Chr. Pupp, *Monatsh. Chem.*, **95**, 633 (1964).

16) E. Nachbaur and A. Engelbrecht, *ibid.*, **95**, 214 (1964).

17) E. E. Kenage, *J. Econ. Entomol.*, **50**, 1 (1957); D. Stewart, *ibid.*, **50**, 7 (1957).

18) Preceding paper: S. Nagase, H. Baba and T. Abe, This Bulletin, **40**, 2358 (1967).

19) U. Wannagat and G. Mennicken, *Z. anorg. allgem. Chem.*, **278**, 310 (1955).

20) S. Nagase, H. Baba and T. Abe, This Bulletin, **38**, 834 (1965).

[*2] Synthesized by the electrochemical fluorination of tri-*n*-butylamine according to the method in the literature; E. A. Kauck and J. H. Simons, U. S. Pat. 2616927 (1952); Brit. Pat. 666733 (1952).

[*3] Gaschro-Kogyo Co., Ltd.,

oxygen difluoride, a mixture of sulfuryl fluoride and sulfur hexafluoride,*4 and thionyl tetrafluoride. When the feed rate was high, unchanged sulfur dioxide appeared after oxygen difluoride. The gases from the sodium fluoride tube were led to and bubbled through an aqueous solution of sodium sulfite containing a small amount of potassium iodide, by which means the products other than sulfuryl fluoride and sulfur hexafluoride were removed.*5 These two products were guided to cold traps and then subjected to low-temperature distillation.

Fluorination of Thionyl Fluoride. An electrolytic cell with a capacity of 300 m*l*[18] was used. Among the several runs made, the best reaction conditions were as follows: thionyl fluoride (36 m*l*/min) and helium (15 m*l*/min) were led through the bubbler into anhydrous hydrogen fluoride containing sodium fluoride (5 g). The electrolysis was then conducted at −30°C with an anodic current density of 1.6 A/dm^2 and at a cell voltage of 6—7 V. However, even under these conditions, explosions in the reaction system frequently occurred and quantitative analyses of the products were not possible. The products consisted of a considerable amount of thionyl tetrafluoride and traces of sulfur hexafluoride and oxygen difluoride.

Fluorination of Thionyl Chloride, Sulfuryl Chloride, Sulfur Mono-, and Dichlorides. For these liquid samples, the fluorination was conducted in batches by the use of the electrolytic cell with a capacity of 1 *l*.[20] A conductivity additive, sodium fluoride (10 g), was necessary for the fluorination of sulfur mono-, and dichlorides. The products obtained from these materials were treated similarly to those obtained from the fluorination of sulfur dioxide. Thionyl tetrafluoride produced from thionyl chloride was yielded as sulfuryl fluoride by hydrolysis.

Results and Discussion

The reaction conditions for the electrochemical fluorination of sulfur dioxide and the results obtained are shown in Table 1. The reaction can be carried out easily; sulfuryl fluoride is produced as the principal product, along with cleaved by-products.

TABLE 1. FLUORINATION OF SULFUR DIOXIDE

Run No.	SO_2 feed[a] rate m*l*/min	Total amount of SO_2 fed, mol	Electricity[b] passed A. hr	Cell temp. °C	SO_2F_2[c] Yield %
1	32	0.201	60	6—7	70.0
2	47	0.312	65	6—7	49.5
3	36	0.239	65	16	90.4
4	30	0.204	50	16—17	64.8

a) He flow rate: 15 m*l*/min.

b) Anodic current density: 2.8 A/dm^2,
Cell voltage: 6—8 V

c) Calculated on the basis of the amount of SO_2 fed.

$$SO_2 \xrightarrow{[F]} SO_2F_2,\ SOF_4,\ SF_6,\ OF_2$$

The sulfur in the products is in the hexavalent state, as is usual in the electrochemical fluorination of sulfur-containing compounds. The composition of the products was not changed practically by the reaction time. A representative example of the composition*6 (Run 1) was sulfuryl fluoride, 62%; thionyl tetrafluoride, 23%; sulfur hexafluoride, 1%; and oxygen difluoride, 14%.

Generally, a lower feed rate with a higher cell temperature gave sulfuryl fluoride in a better yield. Under the conditions used, the highest yield of sulfuryl fluoride was given at a feed rate of 36 m*l*/min and at a cell temperature of 16°C. At this temperature, however, the reaction with the smaller feed rate did not proceed smoothly due to explosions in the apparatus, thus giving a lower yield of sulfuryl fluoride. The cause of the explosions may be the generation of free fluorine because of the insufficient concentration of sulfur dioxide in anhydrous hydrogen fluoride.

The sulfur-oxygen bond in the oxygen-containing sulfur compounds is relatively stable to fluorination, as may be seen in the poor yields (<1%) of sulfur hexafluoride. The sulfur-oxygen bond in sulfuryl fluoride is particularly inert; the thionyl tetrafluoride and sulfur hexafluoride formed from sulfur dioxide are not produced through the exhaustive fluorination of sulfuryl fluoride, which is found not to be fluorinated by the electrochemical fluorination,*7 just as it has been shown not to be fluorinated by the catalytic fluorination.[21]

The electrochemical fluorination of thionyl fluoride resulted in the formation of thionyl tetrafluoride, together with traces of sulfur hexafluoride and oxygen difluoride. However, more highly-fluorinated products such as pentafluorosulfur hypofluorite,[21,22] were not detected.

$$SOF_2 \xrightarrow{[F]} SOF_4,\ (SF_6,\ OF_2)^{*8}$$

The reaction conditions and the yields of the principal products obtained in the electrochemical fluorination of sulfur oxychlorides and sulfur chlorides are shown in Table 2. The several compounds were produced as follows:

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*4 Can be separated by gas chromatography over silica gel.

*5 Thionyl tetrafluoride was converted into sulfuryl fluoride by hydrolysis [H. Jonas, *Z. anorg. allgem. Chem.*, **265**, 273 (1951)].

*6 The ratio of the peak areas in the chromatogram.

*7 The electrochemical fluorination of sulfuryl fluoride was examined by procedures similar to those used for thionyl fluoride. Sulfuryl fluoride was recovered, unchanged.

[21] F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).

[22] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

*8 The amounts of the compounds listed in parentheses in this and in the following equations were small.

TABLE 2. FLUORINATION OF SULFUR COMPOUNDS

Run No.	Sample[a)] mol	Electricity[b)] passed A. hr	Main product Yield[c)] %
5	$SOCl_2$ (0.25)	69	SOF_4 (31.7), SOF_2
6	SO_2Cl_2 (0.25)	97	SO_2F_2 (65.7)
7	S_2Cl_2 (0.125)	155	SF_6 (78.2)[d)]
8	SCl_2 (0.25)	113	SF_6 (63.7)

a) He flow rate: 60 m*l*/min.

b) Anodic current density: 2.8 A/dm², Cell voltage: 5.5—7 V, Cell temperature: 5—6°C.

c) Calculated on the basis of the amount of the starting material charged.

d) A 100% yiled represents the formation of 2 mol of SF_6 from 1 mol of the starting material.

$$SOCl_2 \xrightarrow{[F]} SOF_2,\ SOF_4,\ (SF_6,\ OF_2,\ HCl)$$

$$SO_2Cl_2 \xrightarrow{[F]} SO_2F_2,\ Cl_2,\ (SO_2ClF,\ SF_6,\ OF_2)$$

$$S_2Cl_2 \xrightarrow{[F]} SF_6,\ Cl_2,\ (SOF_2,\ SOF_4)$$

$$SCl_2 \xrightarrow{[F]} SF_6,\ Cl_2,\ (SF_5Cl,\ SOF_2,\ SOF_4)$$

The compositions of the products varied with the reaction time. The amount of sulfur hexafluoride produced from thionyl chloride and sulfuryl chloride was small (1—2% yield). Chlorine in thionyl chloride appeared to be removed mostly as hydrogen chloride,[*9] while in sulfuryl chloride most of the chlorine was removed as chlorine gas.

The electrochemical fluorination of sulfur monochloride which has been briefly described in a patent,[23)] and that of sulfur dichloride afforded sulfur hexafluoride in substantial yields. Traces of thionyl fluoride and thionyl tetrafluoride might be produced from impurities in the sulfur chlorides.

[*9] These oxychlorides are known to react with anhydrous hydrogen fluoride to yield the corresponding oxyfluorides and hydrogen chloride (Ref. 10). This fact was examined under the modified reaction conditions used for the present work; without passing the current through the anhydrous hydrogen fluoride solution in the cell, but with bubbling helium into it, the oxychlorides were subjected to fluorination at 6°C. Thionyl chloride gave thionyl fluoride, while sulfuryl chloride yielded sulfuryl chlorofluoride.

23) M. Prober, U. S. Pat. 2717235 (1955).