The Fluorination of Carbonyl Sulfide[1)]

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The electrochemical fluorination of carbonyl sulfide has been carried out. Carbonyl fluoride and sulfur hexafluoride were obtained as the principal products. The influence of the operating conditions on the reaction has been examined. In addition, a method has been developed for the production of sulfur hexafluoride. This involves the passage of carbon monoxide and sulfur over a catalyst; the resultant gas formed is subsequently introduced into a current-carrying anhydrous hydrogen fluoride in an electrolytic cell. Sulfur hexafluoride was thus obtained in a good yield.

Carbonyl sulfide has been subjected to fluorination by elementary fluorine,2) oxygen difluoride,3) and cobalt trifluoride,4) and has been shown to yield fluorinated cleaved products. The present paper will describe the results of a study of the electrochemical fluorination of carbonyl sulfide. This work was initiated with the hope that the electrochemical process for the fluorination of carbonyl sulfide may produce a fully-fluorinated compound retaining the original sulfur-carbon-oxygen skeleton. However, it was found that, upon electrochemical fluorination, the carbon-sulfur bond in carbonyl sulfide was cleaved, yielding carbonyl fluoride and sulfur hexafluoride as the principal products.

This paper will also deal with a method developed for the production of sulfur hexafluoride, an important commercial sulfur-fluorine compound, by the application of the electrochemical process for the fluorination of gaseous compounds.5) The method involves the passage of a mixture of carbon monoxide and sulfur over a catalyst to convert them into carbonyl sulfide, and then blowing it into a current-carrying anhydrous hydrogen fluoride in an electrolytic cell. This gave sulfur hexafluoride of a relatively high purity in a good yield.

Experimental

Fluorination of Carbonyl Sulfide. Carbonyl sulfide (97.5% min) obtained from the Matheson Co., carbon monoxide (99.5%), ethylene (99.5%), and propylene (99.1%) obtained from the Takachiho Chemical Industrial Co., were used. The other reagents were commercial-grade chemicals. The apparatus used was similar to one described earlier.6) The effective surface area of the anodes and cathodes in an electrolytic cell was 7.7 dm^2. A 450 ml portion of anhydrous hydrogen fluoride was used.

The fluorination was conducted by procedures similar to those used before.5) As an example, the procedures for Run 2 shown in Table 1 will be described. Carbonyl sulfide (25 ml/min) in a cylinder was blown with helium (90 ml/min) through a bubbler into the anhydrous hydrogen fluoride in the cell, while a current was being passed through it at an average anodic current density of 3.0 A/dm^2 at 5.5—6.5 V and at 5—6 °C. It was preferable to use a conductivity additive, sodium fluoride (4 g), for this electrolysis.

The gases generated from the cell were passed through a reflux condenser, a sodium fluoride tube, and were then bubbled into an aqueous solution of sodium sulfite in gas-washing bottles,6) where the carbonyl fluoride in the product was hydrolyzed and converted into carbon dioxide and hydrogen fluoride, and a small amount of oxygen difluoride was removed. The gases were then guided to cold traps kept in ice and in liquid nitrogen.

The collected product, containing subliming compounds (carbon dioxide and sulfur hexafluoride), was first roughly distilled by the use of a low-temperature rectification unit. Each fraction was then analyzed by GC [(Shimadzu GC-1C), column; 0.3 cm *i.d.* × 1.8 m long stainless steel tube packed with 60/80 mesh silica gel, temperature; 80 °C, carrier; helium] as usual. IR measurements [(Hitachi EPI-S2), a gas cell equipped with NaCl windows] were also carried out.

For 3 hrs' operation, a total of 15.7 g (0.262 mol) of carbonyl sulfide was supplied; the following compounds were thus obtained; carbon tetrafluoride (0.4 g, 0.005 mol), sulfur hexafluoride (18.2 g, 0.125 mol), carbon dioxide (4.8 g, 0.109 mol), carbonyl sulfide (7.2 g, 0.120 mol), and trifluoromethyl peroxide (0.6 g, 0.004 mol).

In order to ascertain the composition of the exit gas before contact with water, a sample gas was occasionally withdrawn directly from the sampling valve fixed next to the sodium fluoride tube, and analyzed by GC [(Shimadzu GC-2C), column; for example, 0.3 cm i.d. × 10 m long polytetrafluoroethylene tube packed with Daifl oil ♯3 (Daikin Industries Co.) on 20/80 mesh Shimalite F (Shimadzu Seisakusho Co.), temperature; 0 °C, carrier; helium] and by IR. Special care has been exercised to detect the formation of compounds sensitive to moisture, such as pentafluorosulfur carbonyl fluoride.7)

Preparation of Sulfur Hexafluoride. The apparatus consisted of a molten-sulfur tube, an electrolytic cell, a sodium fluoride tube, gas-washing bottles, and cold traps. Most of these were the same as those used for the fluorination of carbonyl sulfide. They were connected in series. The molten-sulfur tube was made of glass; it was a long-neck (3 cm *i.d.* × 20 cm long), round-bottomed, 50 ml flask fitted with two glass tubings at the top for the inlet and the outlet of gases. The lower end of the inlet tubing was under the surface of the molten sulfur in the flask. About 25 g of sulfur was placed in the bottom, while activated charcoal was packed in the neck of the flask. The gas-washing bottles contained 20% of a sodium hydroxide solution saturated

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1) "Electrochemical Fluorination of Gases," Part VIII.

2) O. Salinovich, E. A. R. de Staricco, and E. H. Staricco, *Inorg. Nucl. Chem. Lett.*, **2**, 157 (1966).

3) D. Soria, E. A. R. de Staricco, and E. H. Staricco, *ibid.*, **5**, 35 (1969).

4) G. A. Silvey and G. H. Cady, *J. Amer. Chem. Soc.*, **74**, 5792 (1952).

5) Part VII of this series: S. Nagase, T. Abe, H. Baba, and K. Kodaira, This Bulletin, **43**, 2980 (1970).

6) S. Nagase, H. Baba, and T. Abe, *ibid.*, **40**, 2358 (1967).

7) R. Czerepinski and G. H. Cady, *J. Amer. Chem. Soc.*, **90**, 3954 (1968).

TABLE 1. FLUORINATION OF CARBONYL SULFIDE

Run No.	COS feed rate (ml/min)	Total amount of COS fed (mol)	Anodic current density (A/dm^2)	Time (min)	Product composition (%)					Yield[a] of fluorinated product (%)			
					CF_4	COF_2	SF_6	COS	$(CF_3O)_2$	CF_4	COF_2	SF_6	$(CF_3O)_2$[b]
1	10	0.170	2.3	360	3.5	41.9	51.7	—	2.8	6.8	80.6	99.4	10.8
2	25	0.262	3.0	240	1.3	30.0	34.4	33.1	1.1	1.9	41.6	47.7	3.1
3	41	0.385	3.0	210	0.9	31.2	22.2	45.5	0.2	1.0	33.9	24.0	0.5

Other conditions: Sodium fluoride added 4 g, helium 90 ml/min, cell voltage 5.5—6.5 V, cell temperature 5—6°C

a) {(Mol of each product)/(mol of COS fed)} × 100.

b) {(Mol of $CF_3OOCF_3 \times 2$)/(mol of COS fed)} × 100.

with sodium sulfite. A small amount of potassium iodide was also added.

In operation, carbon monoxide (19 ml/min) was fed as a blowing gas into the molten-sulfur tube kept at 330 °C in an electric furnace. A mixture of carbon monoxide and sulfur vaporized was passed through an activated charcoal zone, where both elements were converted into carbonyl sulfide, which was subsequently introduced into the current-carrying anhydrous hydrogen fluoride in the cell. (Electrolysis conditions; anhydrous hydrogen fluoride used, 450 ml; sodium fluoride added, 4 g; anodic current density, 3.2 A/dm^2; cell voltage, 6.3—6.5 V; cell temperature, 5—6 °C).

The fluorinated products were passed through the reflux condenser, the sodium fluoride tube, and the gas-washing bottles, and then were led to cold traps immersed in ice and in liquid nitrogen. The sulfur hexafluoride thus obtained, containing small amounts of by-products, was purified as follows. By the use of the low-temperature rectification unit, carbon tetrafluoride was distilled at -128—-126 °C at atmospheric pressure (fraction 1); then the top of the column was kept at -65— -60 °C, and sulfur hexafluoride was taken out at 700—750 mmHg (fraction 2). Bistrifluoromethyl peroxide and sulfuryl fluoride remained in the column. It was possible to remove completely a trace of sulfuryl fluoride in the sulfur hexafluoride by passing fraction 2 through a glass tube (3 cm *i.d.* × 40 cm long) containing 5/7 mesh silica gel.

After 4 hrs' operation, 6.1 g (0.190 g.atom) of sulfur was vaporized from the sulfur-molten tube, and 25.8 g (0.177 mol) of sulfur hexafluoride (purity, 99.9%) was thus obtained (yield 93.2%), together with small amounts of carbon tetrafluoride, bistrifluoromethyl peroxide, and sulfuryl fluoride. Ethylene, propylene, and carbonyl chloride were also examined as blowing gases. The experiments for the preparation of sulfur hexafluoride from these starting materials were conducted much as in the case of carbon monoxide.

Results and Discussion

The fluorination of carbonyl sulfide resulted in the cleavage of the carbon-sulfur bond:

$$COS \xrightarrow{[F]} CF_4,\ COF_2,\ SF_6,\ CF_3OOCF_3$$

The reaction conditions and results obtained are shown in Table 1. If the carbon-sulfur bond was not cleaved completely, such a compound as pentafluorosulfur carbonyl fluoride[7] would be obtained. In this work, even under the preferred conditions for milder fluorination[8] of gaseous compounds (the higher feed rate used in Run 3), the cleavage of the carbon-sulfur bond occurred. A low-temperature fluorination also yielded fragmented products; feed rate, 35 ml/min; cell temperature, -25 °C; product composition (mol %), carbon tetrafluoride (0.9), carbonyl fluoride (58.8), sulfur hexafluoride (18.8), carbonyl sulfide (21.1), and bistrifluoromethyl peroxide (0.3).

Under severe fluorination conditions (Run 1), a considerable amount of bistrifluoromethyl peroxide was obtained. The formation of this may be explained in terms of the coupling of two trifluoromethoxy radicals, most likely produced by the attachment of a fluorine radical to the carbonyl fluoride formed in the course of the fluorination.

In contrast to the carbon-sulfur bond, the carbon-oxygen bond was rather stable to the electrochemical fluorination,[5] as is shown by the kinds and amounts of fluorinated products formed. The bonding energy for the carbon-oxygen bond in carbonyl sulfide is much greater than that for the carbon-sulfur bond.[9] This may be the primary cause for the present results. Salinovich *et al.*[2] examined the reaction of carbonyl sulfide with elementary fluorine under a variety of operating conditions and observed a very rapid reaction, which gave carbonyl fluoride and sulfur hexafluoride. Earlier Silvey and Cady[4] obtained similar results in the fluorination of carbonyl sulfide with cobalt trifluoride. From these observations,[2,4] together with the present results described above, it may be stated that it is difficult to fluorinate carbonyl sulfide and still totally retain the sulfur-carbon-oxygen skeleton by direct methods of fluorination.

The process described herein for the preparation of sulfur hexafluoride can be expressed as follows:

$$CO \xrightarrow{S} COS \xrightarrow{[F]} COF_2,\ SF_6 \xrightarrow{\text{Alkali}} SF_6$$

Because it is of commercial importance, sulfur hexafluoride has been prepared by a number of methods. An electrochemical process was often employed.[10] In the present method, the starting material is elemental

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[8] S. Nagase, K. Tanaka, and H. Baba, This Bulletin, **38**, 834 (1965).

[9] Landolt-Börnstein, "Zahlenwerte und Funktionen," 6 Auflage, 1 Band, 2 Teil (1951), p. 38.

[10] a) M. Prober, U. S. Pat. 2717235 (1955). b) E. H. Man, U. S. Pat. 2904476 (1959). c) P. Sartori, *Angew. Chem.*, **75**, 417 (1963). d) M. Hisasue, N. Watanabe, and S. Yoshizawa, *Asahi Garasu Kenkyu Hokoku*, **15**, 127; 139 (1965). e) L. Heinrich, *Z. Anorg. Allgem. Chem.*, **346**, 44 (1966). f) P. E. Ashley, J. D. La Zerte, and R. J. Seffl, U. S. Pat. 3345277 (1967). g) T. Abe, S. Nagase, K. Kodaira, and H. Baba, This Bulletin, **43**, 1812 (1970). h) J. Nakamura, S. Sato, and Y. Omote, Japan Pat. Publication No. 45—32525 (1970).

sulfur, and the fluorination proceeds smoothly. Although the process involves the loss of carbonyl fluoride, it affords sulfur hexafluoride of high purity in a good yield (93.2%).

The action of carbon monoxide upon sulfur is known to produce carbonyl sulfide.[11] The method described in the Experimental Section was also efficient in converting carbon monoxide into carbonyl sulfide. For example, when the feed rate of carbon monoxide was 19 ml/min, the conversions were as follows: 72% at 250 °C, 88% at 280 °C, and 97% at 300 °C. The conditions for 100% conversion (at 330 °C) were applied for the run illustrated in the Experimental Section.

When ethylene or propylene was used as the blowing gas instead of carbon monoxide, they were converted into carbon disulfide and hydrogen sulfide.[12] The amount of the olefin introduced with helium into the molten-sulfur tube was so adjusted that it reacted almost completely with the sulfur. The activated charcoal was again used as the catalyst for this reaction. The whole process can be represented by the following formulae:

$$CH_2{=}CH_2 \xrightarrow[320^\circ C]{S} CS_2,\ H_2S$$

$$\xrightarrow{[F]} SF_6(CF_4,\ C_2F_6,\ CF_3SF_5,\ C_2F_5SF_5,\ SO_2F_2,\ CS_2)$$

$$CH_3CH{=}CH_2 \xrightarrow[350^\circ C]{S} CS_2,\ H_2S$$

$$\xrightarrow{[F]} SF_6(CF_4,\ C_2F_6,\ CF_3SF_5,\ C_3F_8,\ SO_2F_2)$$

In the case of ethylene,[13] some representative results obtained were as follows: composition of the product (mol %): carbon tetrafluoride (13.5), hexafluoroethane (1.0), sulfur hexafluoride (68.9), trifluoromethylsulfur pentafluoride (13.3), pentafluoroethylsulfur pentafluoride (0.5), sulfuryl fluoride (0.8), and carbon disulfide unchanged (2.0); the yield[14] of sulfur hexafluoride (20.0 g, 0.137 mol) was 39.2%. A small amount of sulfur was found in the electrolytic cell.

In the case of propylene,[15] the products were carbon tetrafluoride (6.9), hexafluoroethane (1.0), sulfur hexafluoride (82.1), trifluoromethylsulfur pentafluoride (4.5), octafluoropropane (4.3), and sulfuryl fluoride (1.1), and the yield[14] of sulfur hexafluoride (23.0 g, 0.158 mol) was 63.2%.

Carbonyl chloride was also useful as a blowing gas. The whole process may be described as follows:

$$COCl_2 \xrightarrow[360\ ^\circ C]{S} COS,\quad S_2Cl_2 \xrightarrow{[F]} SF_6(COF_2,\ COS)$$

The products[16] were carbonyl fluoride (41.1), sulfur hexafluoride (45.0), and carbonyl sulfide (13.9), and the yield[14] of sulfur hexafluoride (26.3 g, 0.180 mol) was 73.2%. As far as the preparation of sulfur hexafluoride is concerned, the process using carbon monoxide is superior to all others among those studied in the present work.

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11) For example, R. J. Ferm, *Chem. Rev.*, **57**, 621 (1957).

12) S. Oae, "Yūki-iō-kagōbutsu no Kagaku," Vol. 1, Kagaku Dojin, Kyoto (1968), p. 24.

13) Conditions: Sulfur consumed, 11.2 g (0.349 g. atom); sodium fluoride added, 4 g; anodic current density, 3.2 A/dm^2; cell voltage, 6.5—7.5 V; electricity passed through, 99 A·hr; cell temperature, 6—7 °C.

14) Based on the amount of sulfur (g. atom) vaporized from the molten–sulfur tube.

15) Conditions: Sulfur consumed, 8.0 g (0.250 g. atom); sodium fluoride added, 4 g; anodic current density, 2.9 A/dm^2; cell voltage, 6.0—7.9 V; electricity passed through, 88 A·hr; cell temperature, 6—7 °C.

16) Conditions: Sulfur consumed, 7.9 g (0.246 g. atom); sodium fluoride added, 4 g; anodic current density, 3.2 A/dm^2; cell voltage, 6.1—7.2 V; electricity passed through, 96 A·hr; cell temperature, 6—7 °C.