307. *Synthesis of Pentafluorosulphur Chloride and Sulphur Oxide Tetrafluoride in the Microwave Discharge.*

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The products of the decomposition of sulphur hexafluoride, disulphur decafluoride, and sulphur tetrafluoride in the microwave discharge have been identified. Reaction of these fluorides with chlorine in the discharge produces pentafluorosulphur chloride. Their reaction with oxygen leads to sulphur oxide tetrafluoride and sulphuryl fluoride.

The high-frequency discharge produced by a microwave source has been used previously in the synthesis of diboron tetrachloride from boron trichloride [1] and of digermanium hexachloride from germanium tetrachloride.[2] During our work a study of the decomposition of sulphur tetrafluoride was also published.[3] The technique is at present of interest primarily as a preparative method. Its chief limitations are the relatively high temperature of the reaction zone and the difficulty of unravelling reaction mechanisms in view of the large number of species produced in the discharge. The relatively high thermal stability of sulphur fluorides does, however, offer some prospect of overcoming the first of these limitations.

In preliminary experiments it was found that sulphur hexafluoride underwent little change in the discharge. The infrared spectrum of the product showed peaks due to sulphuryl fluoride [4] and sulphur oxide tetrafluoride,[5] as well as silicon tetrafluoride, formed by attack on the silica discharge tube. They were present in all experiments made with a silica tube. These were eliminated by using a Teflon discharge tube which, however, could be operated without overheating only at a low power input (<50 watts), where it sometimes became difficult to maintain the discharge. Disulphur decafluoride gave sulphur hexafluoride as the main product. It was separated from unchanged disulphur decafluoride by fractionation *in vacuo* and weighed with traces of sulphuryl fluoride and sulphur oxide tetrafluoride. A typical yield is shown in Table 1.

Table 1.

Compound	Flow rate (10^{-3} mole/hr.)	Power input (watts)	Conversion (%)	Yield/hr. (10^{-3} mole)
S_2F_{10}	5·8	80	69 (to SF_6)	4·0 (SF_6)
SF_4	20·9	80	—	2·5 (S), 2·4 (SF_6)
$(SF_5)_2O_2$	3·93	80	—	1·66 (SF_4O), 0·7 (SF_6)
SeF_6	5·44	120	1·95	0·13 (SeF_4)

Sulphur tetrafluoride gave sulphur and sulphur hexafluoride as the main products, in agreement with the results of Smith and Engelhardt.[3] Decomposition of pentafluorosulphur chloride yielded sulphur hexafluoride and chlorine, both of which were characterised; and bis(pentafluorosulphur) peroxide gave sulphur hexafluoride, and sulphur oxide tetrafluoride as major products. Selenium hexafluoride gave selenium tetrafluoride as the main product.

Pentafluorosulphur chloride was formed in the reactions of sulphur tetrafluoride and hexafluoride and of disulphur decafluoride with chlorine. Sulphur tetrafluoride also gave sulphur hexafluoride. Typical yields with a 1 : 1 mixture of reactants are shown in Table 2. Products with a ratio of F : S lower than in the original compound were not detected with the analytical procedure used. The conversion of sulphur hexafluoride into pentafluorosulphur chloride increased with the molar proportion of chlorine and

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[1] Frazer and Holzman, *J. Amer. Chem. Soc.*, 1958, **80**, 2907.
[2] Shriver and Jolly, *J. Amer. Chem. Soc.*, 1958, **80**, 6692.
[3] Smith and Engelhardt, *J. Amer. Chem. Soc.*, 1960, **82**, 3838.
[4] Perkins and Wilson, *J. Chem. Phys.*, 1952, **20**, 1791.
[5] Dudley, Cady, and Egers, Jr., *J. Amer. Chem. Soc.*, 1956, **78**, 1553.

the yield, calculated for a constant flow rate of the combined reactants, was a maximum with the two compounds in equimolar amounts. Results are shown in Table 3 (power input 50 watts). A Teflon discharge tube was used in this series of experiments, but it was found in a series of runs under comparable conditions that, within the accuracy of the analytical methods, yields were independent of whether Teflon or silica was used.

TABLE 2.

Flow rate (SF_4, 10^{-2} mole/hr.)	Power input (watts)	Conversion into SF_5Cl (%)	Yield of SF_5Cl (10^{-3} mole/hr.)	Yield of SF_6 (10^{-3} mole/hr.)
0·17	80	31	0·53	0·055
0·48	60	15	0·74	0·027

TABLE 3.

Flow rate (SF_6, 10^{-2} mole/hr.)	Molar ratio $SF_6 : Cl_2$	Conversion into SF_5Cl (%)	Yield of SF_5Cl (10^{-3} mole/hr.)
2·35	15·6 : 1	3	0·74
1·81	5·9 : 1	6	1·03
1·06	0·99 : 1	12	1·24
0·28	0·17 : 1	25	0·70

The percentage conversion with a 1 : 1 mixture increased as the flow rate decreased, though the yield of pentafluorosulphur chloride (g./hr.) was a maximum at a flow rate of $\sim$0·5 mole/hr. of sulphur hexafluoride. The results in Table 4 were obtained with a power input of 80 watts (silica discharge tube). Although the fact that the maximum yield occurs with a 1 : 1 mixture suggests that the reaction is $SF_6 + Cl_2 \longrightarrow SF_5Cl + ClF$, no chlorine monofluoride was isolated, owing probably to its ready reaction with glass in the vacuum-fractionation apparatus.

TABLE 4.

Flow rate, SF_6 (10^{-2} mole/hr.)	10·06	3·50	0·98	0·45	0·15
Conversion into SF_5Cl (%)	2	10	16	25	28
Yield of SF_5Cl (10^{-3} mole/hr.)	1·97	3·59	1·61	1·12	0·42

The yield of pentafluorosulphur chloride decreased roughly in proportion to the amount of oxygen added to a 1 : 1 mixture of sulphur hexafluoride and chlorine. It was shown qualitatively from the infrared spectra of the products that oxygen increased the proportion of oxyfluorides, formation of which by a competing reaction is proved by observations recorded below. Typical results are given in Table 5 (power input 80 watts).

TABLE 5.

Flow rate of SF_6 (SF_6, 10^{-2} mole/hr.)	O_2 (moles %)	Conversion into SF_5Cl (%)		Yield of SF_5Cl (10^{-3} mole/hr.)	
		with O_2	without O_2	with O_2	without O_2
0·55	3·2	19	24	1·03	1·32
0·66	8·8	10	23	0·66	1·51
0·67	22·4	5	23	0·35	1·52

TABLE 6.

Power input (watts)	Flow rate (10^{-2} mole/hr.)	Conversion into SF_5Cl (%)	Yield of SF_5Cl (10^{-3} mole/hr.)	Yield of SF_6 (10^{-3} mole/hr.)
80	0·21 (S_2F_{10})	21	0·87	0·66
40	0·21 (S_2F_{10})	9	0·40	0·30
80	0·17 (SF_4)	31	0·53	0·055
60	0·48 (SF_4)	15	0·74	0·027

Reaction of disulphur decafluoride with chlorine in the discharge gave pentafluorosulphur chloride and sulphur hexafluoride as the main products. Typical yields for a 1 : 1 mixture are shown in Table 6 (power input 80 watts). Products with a ratio F : S lower than in the original compound were not detected with the analytical procedure used.

Experiments with a 1 : 1 mixture of sulphur tetrafluoride and chlorine gave the same main products (Table 2), but the proportion of hexafluoride was considerably less.

Reaction of bispentafluorosulphur peroxide gave no pentafluorosulphur chloride: the main products, identified by gas chromatography and infrared spectroscopy, were sulphur oxide tetrafluoride and thionyl fluoride.

The only product detected in the reaction of selenium hexafluoride with chlorine in the discharge was selenium tetrafluoride and no chlorofluoride was found. It is possible, however, that pentafluoroselenium chloride could be made in the low-temperature glow discharge.

TABLE 7.

Compound	Molar ratio, Compound : O_2	Flow rate (10^{-2} mole/hr.)	Approx. yield of SF_4O (10^{-2} mole/hr.)	Conversion into SF_4O (%)
SF_6	1·32 : 1	0·61	0·11	18
S_2F_{10}	0·94 : 1	0·17	0·19	57
SF_5Cl	1·15 : 1	0·93	0·01	1·3

Typical results of reaction of sulphur hexafluoride, disulphur decafluoride, and pentafluorosulphur chloride with oxygen are shown in Table 7. Sulphur oxide tetrafluoride was formed; quantities were in considerable excess of the amount that could be formed by attack on the quartz tube. The decafluoride and pentafluorosulphur chloride also gave small amounts of hexafluoride, and sulphuryl fluoride was produced in each case. The power input was 80 watts. The relatively low yield of sulphur oxide tetrafluoride from pentafluorosulphur chloride is notable.

The appearance potentials for the positive ions SF_5^+, SF_4^+, SF_3^+, SF_2^+, SF^+, and S^+ from SF_6 measured by Dibeler and Mohler [6] were in the range 15·9 ev for SF_5^+ to 37·3 ev for S^+, the relative abundances of SF_5^+, SF_4^+, and SF_3^+ for electron energies of 50 ev being 100 : 8·9 : 27·6. The other species had abundances ranging from 8·6 for SF^+ to 5·6 for S^+. The doubly charged ions SF_4^{2+}, SF_2^{2+}, and SF_3^{2+} were less abundant. The negative ions SF_6^-, SF_5^-, F^-, and F_2^- also appear in a narrow but lower range of electron energies.[7] Conditions in the discharge are probably such as to give all of these ions. The small amount of decomposition in sulphur hexafluoride must be due to recombination and to the inherent thermal stability of the hexafluoride. Reactions leading to pentasulphur chloride, sulphur oxide tetrafluoride, or sulphuryl fluoride, which occur on the addition of a second reactant, can be accounted for qualitatively by reaction of the more abundant species to give products of moderate thermal stability. A detailed analysis of the mechanism is not, however, possible on the results obtained.

EXPERIMENTAL

Sulphur hexafluoride and tetrafluoride, disulphur decafluoride, pentafluorosulphur chloride, and bispentafluorosulphur peroxide, made available from a commercial source, were purified by vacuum-fractionation. Selenium hexafluoride was prepared from selenium and fluorine and purified by the standard method. The apparatus was a flow system connected directly to the vacuum-fractionation apparatus. Reactant mixtures were fed to the discharge from a 4-l. storage bulb, the pressure in which did not change appreciably during the duration of a run (*ca.* 15 min.). Flow rates were determined by introducing weighed quantities of the fluoride and of chlorine where appropriate into the 4-l. bulbs after weighing them in a 500-ml. bulb, and then reweighing them in the small bulb after the run. Oxygen additions were made manometrically to the 4-l. bulb. Flow was controlled by two fine-adjustment valves, and the overall pressure in the region of the discharge tube (*ca.* 2 mm. Hg) was measured on a butyl phthalate manometer. All taps were lubricated with KelF grease.

The silica discharge tube was 30 cm. long and of 9 mm. internal diameter and was fitted with standard tapers. The Teflon discharge tube (30 cm. long, of 15 mm. external and 6 mm.

[6] Dibeler and Mohler, *J. Res. Nat. Bur. Stand.*, 1948, **28**, 40.
[7] Hearn and Hannay, *J. Chem. Phys.*, 1953, **21**, 119.

internal diameter) was sealed to Pyrex by a vacuum-tight cement. The discharge tube passed axially through a cylindrical resonance cavity, power to which was passed by a coaxial cable from a medical therapy unit operating at a frequency of 2425 megacycles/sec. The power output was variable from 0 to 200 watts. The resonance cavity was a silver-plated, hollow, brass cylinder (of 8·9 cm. internal diameter, and 3·2 cm. internal depth) with circular holes at the top and bottom through which the discharge tube passed. The main adjustment for tuning was a threaded collar fitted to the top orifice. This could be moved up and down the axis of the cylinder. Two 12-mm. tuning screws protruded through the sides of the cylinder at opposite ends of a diameter. These could be screwed in or out to produce resonance. The power input to the cavity was by coaxial cable to a wire loop. This passed from the centre of the cable and was silver-soldered to the body of the cavity, which was itself in electrical contact with the outer sheath of the cable. The tuning of the resonance cavity was done roughly by eye, the brightness of the discharge being used as an indication of the approach to resonance. A more reliable method was to use a detector circuit to measure the power going into the cavity. This circuit consisted of a wire loop connected through a crystal rectifier to a D.C. milliammeter. Power passing into the cavity was picked up by the loop and indicated as a current. The three variable screws were then adjusted systematically until the current was a maximum. A small orifice in the side of the cylinder served for observation and also to cool the discharge tube during operation by permitting air to be blown in.

The infrared spectra of all the reactants and products are known and this criterion was used in identification, usually coupled with removal of the readily hydrolysable products. Gas chromatography was also used to identify the main species. The relative retention times measured on a 2-m. column of di-isodecyl phthalate supported on " Celite 535," with oxygen-free nitrogen as carrier gas at a flow rate of 40 ml./min. were: $SF_6 : SF_5Cl$, 1 : 1·6; $SF_6 : SF_5Cl : SF_4$, 1 : 1·4 : 2·7; $SF_6 : SF_5Cl : SOF_2$, 1 : 1·7 : 5·7; $SF_6 : SOF_4 : SOF_2$, 1 : 1·5 : 1·6.

In the reaction of sulphur hexafluoride with chlorine the product was treated with iodine to remove free chlorine as iodine monochloride. The volatile residue was shaken with dilute sulphuric acid to remove thionyl fluoride, sulphur oxide tetrafluoride, and silicon tetrafluoride. Pentafluorosulphur chloride and sulphur hexafluoride and a trace of sulphuryl fluoride (shown by gas chromatography) remained. This mixture was dried by passage through a trap at −95° and weighed. It was then hydrolysed with 10% aqueous sodium hydroxide, which decomposes only pentafluorosulphur chloride. The residue of sulphur hexafluoride together with the small amount of sulphuryl fluoride was dried and weighed. No correction was made in the recorded data for the sulphuryl fluoride content. Gravimetric determination of chloride in the hydrolysate gave the amount of pentafluorosulphur chloride and determination of sulphur as sulphate enabled its identity to be established (Found: S, 21·2; Cl, 20·6. Calc. for ClF_5S: S, 19·7; Cl, 21·8%). Analysis of pentafluorosulphur chloride from the reaction of disulphur decafluoride with chlorine gave S, 20·7; Cl, 20·6%. All other estimates of the yield of pentafluorosulphur chloride were based on acid hydrolysis to remove traces of thionyl tetrafluoride, followed by vacuum-fractionation, hydrolysis of a weighed sample of the pentafluorosulphur chloride fraction and determination of chloride in the hydrolysate. Sulphur oxide tetrafluoride was estimated by acid hydrolysis and determination of the sulphate content of the hydrolysate.

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