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Improved Methods for the Synthesis of SF_5OSF_5 and $SF_5O_2SF_5$

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Sulfur hexafluoride is widely used as an inert dielectric in a variety of electrical devices.[1] In the event of an electrical discharge, SF_6 can give rise to a variety of byproducts including some sulfur oxyfluorides when oxygen sources are present. Pure calibration standards of these byproducts are necessary for detailed analysis of such systems. Recent requests for pure samples of bis(pentafluorosulfur) oxide, SF_5OSF_5, and bis(pentafluorosulfur) peroxide, $SF_5O_2SF_5$, prompted us to develop a new method for the synthesis of SF_5OSF_5 and to improve a previously reported method for the synthesis of SF_5OOSF_5.

Bis(pentafluorosulfur) oxide has been prepared previously by the thermal reactions of SF_5OF with SF_4[2,3] and by photochemical reactions of SF_5Cl with oxygen[4] and of SF_4 with OF_2.[5] The yields are low, and the SF_5OSF_5 obtained is difficult to separate from the coproduct SF_5OOSF_5.

Bis(pentafluorosulfur) peroxide was first observed in very low yield as a byproduct in the fluorination of sulfur in the presence of oxygen.[6] Subsequently, photochemical reactions of SF_5Cl with O_2,[4,7] photolysis of SF_5OF[8] or SF_5OCl,[9] and thermal reactions of SF_5OF with SOF_2 or OSF_4 were used to prepare the peroxide.[2,8] The photochemical reactions of SF_5Cl and SF_5OCl are high-yield methods for the preparation of SF_5OOSF_5, but varying amounts of SF_5OSF_5 are present in the peroxide prepared by these methods and the oxide can only be removed by efficient fractional distillation or gas chromatography.

In this paper we report high-yield preparations of pure SF_5OSF_5 and SF_5OOSF_5 from the readily available starting materials OSF_2, SF_4, ClF, and F_2.

Experimental Section

Reagents. The starting materials OSF_2, SF_4, F_2, and Cl_2 were obtained from commercial sources and used as received. Chlorine monofluoride was prepared by reaction of Cl_2 with fluorine in a Monel bomb at 250 °C.[10] SF_5OSF_4 was prepared by reaction of F_2 with SOF_2 at 22 °C.[11] Pentafluorosulfur chloride was prepared by reaction of SF_4 with ClF using a CsF catalyst.[12] Pentafluorosulfur hypochlorite was prepared by the CsF-catalyzed reaction of OSF_4 with ClF.[13] Pentafluorosulfur hypofluorite was prepared by reaction of OSF_4 with F_2 over a CsF catalyst.[11,14]

Synthesis of SF_5OSF_5. Pentafluorosulfur chloride (15.1 mmol) and SF_5OCl (12.1 mmol) were added by vacuum transfer to a 1.0-L Pyrex photochemical reaction vessel fitted with a quartz insert. The insert was water cooled and held a 200-W Hanovia medium-pressure mercury lamp. The mixture was irradiated for 4 h at 22 °C, and the reaction products were collected under dynamic vacuum in a −196 °C trap. The products were then separated by fractional condensation through traps kept at −111 and −196 °C. The −111 °C trap contained a mixture of SF_5OSF_5 and SF_5OOSF_5 (9.6 mmol) which was then vacuum-transferred into a copper reactor of ~5.0-mL volume that was fitted with a brass valve. The reactor had been passivated with fluorine. The mixture of SF_5OSF_5/SF_5OOSF_5 was then heated at 237 °C for 2.5 h followed by fractional condensation through traps held at −118 and −196 °C. The −118 °C trap contained pure SF_5OSF_5 (9.2 mmol, 72% based on SF_5OCl), and the −196 °C trap contained 0.3 mmol of a mixture of SO_2F_2, SOF_4, and SF_6. The properties of SF_5OSF_5 (bp,[5] IR[4]) agreed with literature values.

Table I

run	conditions (°C, h)	amt of $SF_5O_2SF_5$ (mmol)	cumulative yield (%)[d]
1[a]	163, 22	2.61	41.4
2[b]	170, 4	0.84[c]	55.0
3[b]	170, 17	1.49[c]	78.8
4[b]	170, 22	0.37[c]	84.7
5[b]	199, 100	0.13[c]	87.0

[a] 6.3 mmol of SF_5OF, 7.3 mmol of SOF_4. [b] Unreacted starting materials from previous run. [c] Additional $SF_5O_2SF_5$. [d] Based on starting SF_5OF.

Synthesis of SF_5OOSF_5. Pentafluorosulfur hypofluorite (6.3 mmol) and SOF_4 (7.3 mmol) were added by vacuum transfer to a 5-mL copper reactor as described above for SF_5OSF_5. The reactor was warmed from −196 to +22 °C and then heated to 163 °C for 22 h. The contents were then collected at −196 °C under dynamic vacuum and separated by fractional condensation through traps held at −112 and −196 °C. SF_5OOSF_5 was retained in the −112 °C trap, and unreacted starting materials along with very small amounts of SO_2F_2 and SF_6 were retained in the −196 °C trap. The contents of the −196 °C trap were returned to the copper reactor, and this cycle was repeated several times. The data are summarized in Table I.

After run 5, no unreacted SF_5OF was detectable by IR after separation of SF_5OOSF_5. The IR of $SF_5O_2SF_5$ agreed with literature values.[8,14] The physical properties determined were slightly different from literature values: bp = 47.3 °C (49.4 °C[8]), mp = −93.8 °C (−95.4 °C[8]).

Results and Discussion

The formation of SF_5OSF_5 by photolysis of a mixture of SF_5OCl and SF_5Cl presumably results from a combination of $SF_5^{\bullet}$ and $SF_5O^{\bullet}$ radicals by direct combination and by radical abstraction reactions as shown in the following simplified equations.

$$SF_5OCl \xrightarrow{h\nu} SF_5O^{\bullet} + Cl^{\bullet}$$

$$SF_5Cl \xrightarrow{h\nu} SF_5^{\bullet} + Cl^{\bullet}$$

$$SF_5^{\bullet} + SF_5OCl \rightarrow SF_5OSF_5 + Cl^{\bullet}$$

$$SF_5O^{\bullet} + SF_5Cl \rightarrow SF_5OSF_5 + Cl^{\bullet}$$

$$SF_5O^{\bullet} + SF_5^{\bullet} \rightarrow SF_5OSF_5$$

Previous results on the photolysis of SF_5OCl and SF_5Cl/O_2 indicate that SF_5OSF_5 and $SF_5O_2SF_5$ are formed in varying ratios depending on the reaction conditions.[4,7,9] In the case of SF_5Cl/O_2, the peroxide is the major product when it is continuously removed from the reaction mixture, whereas, in a static system, SF_5OSF_5 is the major product. In the case of SF_5OCl, the peroxide is the major product under all conditions reported, but the amount of SF_5OSF_5 increases with irradiation time. The low yield of peroxide in this work implies an efficient radical abstraction reaction between $SF_5O^{\bullet}$ and SF_5Cl and/or $SF_5^{\bullet}$ and SF_5OCl. The maximum yields of SF_5OSF_5 approached 85% based on SF_5OCl, making this synthesis the highest yield method by a

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(1) *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed.; Interscience Publishers: New York, 1966; Vol. 9, p 664.
(2) Williamson, S. M.; Cady, G. H. *Inorg. Chem.* **1962**, *1*, 673.
(3) Roberts, H. L. *Inorg. Chem.* **1963**, *2*, 1016.
(4) Roberts, H. L. *J. Chem. Soc.* **1960**, 2774.
(5) Oberhammer, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1435.
(6) Harvey, R. B.; Bauer, S. H. *J. Am. Chem. Soc.* **1954**, *76*, 859.
(7) Witucki, E. F. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 437.
(8) Merrill, C. I.; Cady, G. H. *J. Am. Chem. Soc.* **1961**, *83*, 298.
(9) Schack, C. J.; Christe, K. O. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 293.
(10) Tari, I.; DesMarteau, D. D. *J. Org. Chem.* **1980**, *45*, 1214.
(11) Ruff, J. K. *Inorg. Synth.* **1968**, *11*, 131.
(12) Tullock, C. W.; Coffman, D. D.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 357.
(13) (a) Schack, C. J.; Wilson, R. D.; Muirhead, J. S.; Cohz, S. N. *J. Am. Chem. Soc.* **1969**, *91*, 2907. (b) Gould, D. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1310.
(14) Dudley, F. B.; Cady, G. H.; Eggers, D. F., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 1553.
(15) Carter, H. A.; Shreeve, J. M. *Spectrochim. Acta* **1973**, *29A*, 1321.

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large margin. Increasing the ratio of SF_5Cl to SF_5OCl did not result in higher yields of SF_5OSF_5.

The removal of $SF_5O_2SF_5$ from SF_5OSF_5 was readily accomplished as suggested by Seppelt,[5] by heating the mixture to decompose the peroxide to SF_6, SO_2F_2, SOF_4, and O_2, which are easily removed from the remaining SF_5OSF_5. A surprising result was observed in this purification process: both SF_5OSF_5 and $SF_5O_2SF_5$ are rapidly decomposed in a 304 stainless steel vessel above 200 °C, whereas, in copper or Monel 400, only $SF_5O_2SF_5$ is thermolyzed. The reason for this difference in behavior is not obvious. Seppelt used a Monel vessel in preparing pure SF_5OSF_5.

The preparation of $SF_5O_2SF_5$ free of SF_5OSF_5 is more challenging than the reverse situation. We explored numerous literature methods and found that all gave the peroxide contaminated with the oxide, except for the work of Merrill and Cady that used a static system involving SOF_2 and SF_5OF.[8] We found that this method could be considerably improved by using SOF_4 in place of SOF_2. Merrill and Cady had also utilized these reactants in a flow system over AgF_2 and Williamson and Cady[2] had utilized these reactants in a static system over AgF_2, but the uncatalyzed reaction of SOF_4 and SF_5OF has previously not been reported. However in reactions of SF_5OF with SOF_2, OSF_4 is surely an intermediate as suggested by Merrill and Cady.[8] By recycling the unreacted SOF_4 and SF_5OF (Table I), we obtained an 87% yield of the peroxide. These results suggest that there is an equilibrium between these reactants in much the same way that a mixture of the related CF_3OF and COF_2 are in equilibrium with the peroxide CF_3OOCF_3.[16]

$$CF_3OF + COF_2 \overset{>225\ ^\circ C}{\rightleftharpoons} CF_3OOCF_3$$

$$SF_5OF + SOF_4 \overset{160\text{–}200\ ^\circ C}{\rightleftharpoons} SF_5OOSF_5$$

For a given amount of starting SF_5OF and SOF_4, the concentration of SF_5OOSF_5 reaches an apparent steady state at a fixed temperature, although no effort was made to examine this in detail.[17]

In summary, improved methods for the synthesis of pure SF_5OSF_5 and $SF_5O_2SF_5$ have been developed to provide standards for the analysis of the products of electrical breakdown in devices employing SF_6 as an insulating gas.

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(16) Porter, R. S.; Cady, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 5628.

(17) A reviewer pointed out that this may be a case of a slow reaction of SF_5OF with OSF_4 and a competing slow decomposition of $SF_5O_2SF_5$. We have not shown that $SF_5O_2SF_5$ does indeed decompose to SF_5OF and SOF_4. This was beyond the scope of this work.