

## Improved Methods for the Synthesis of SF<sub>5</sub>OSF<sub>5</sub> and SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub>

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Sulfur hexafluoride is widely used as an inert dielectric in a variety of electrical devices.<sup>1</sup> In the event of an electrical discharge, SF<sub>6</sub> 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<sub>5</sub>OSF<sub>5</sub>, and bis(pentafluorosulfur) peroxide, SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub>, prompted us to develop a new method for the synthesis of SF<sub>5</sub>OSF<sub>5</sub> and to improve a previously reported method for the synthesis of SF<sub>5</sub>OOSF<sub>5</sub>.

Bis(pentafluorosulfur) oxide has been prepared previously by the thermal reactions of SF<sub>5</sub>OF with SF<sub>4</sub>,<sup>2,3</sup> and by photochemical reactions of SF<sub>5</sub>Cl with oxygen<sup>4</sup> and of SF<sub>4</sub> with OF<sub>2</sub>.<sup>5</sup> The yields are low, and the SF<sub>5</sub>OSF<sub>5</sub> obtained is difficult to separate from the coproduct SF<sub>5</sub>OOSF<sub>5</sub>.

Bis(pentafluorosulfur) peroxide was first observed in very low yield as a byproduct in the fluorination of sulfur in the presence of oxygen.<sup>6</sup> Subsequently, photochemical reactions of SF<sub>5</sub>Cl with O<sub>2</sub>,<sup>4,7</sup> photolysis of SF<sub>5</sub>OF<sup>8</sup> or SF<sub>5</sub>OCl,<sup>9</sup> and thermal reactions of SF<sub>5</sub>OF with SOF<sub>2</sub> or OSF<sub>4</sub> were used to prepare the peroxide.<sup>2,8</sup> The photochemical reactions of SF<sub>5</sub>Cl and SF<sub>5</sub>OCl are high-yield methods for the preparation of SF<sub>5</sub>OOSF<sub>5</sub>, but varying amounts of SF<sub>5</sub>OSF<sub>5</sub> 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<sub>5</sub>OSF<sub>5</sub> and SF<sub>5</sub>OOSF<sub>5</sub> from the readily available starting materials OSF<sub>2</sub>, SF<sub>4</sub>, ClF, and F<sub>2</sub>.

### Experimental Section

**Reagents.** The starting materials OSF<sub>2</sub>, SF<sub>4</sub>, F<sub>2</sub>, and Cl<sub>2</sub> were obtained from commercial sources and used as received. Chlorine monofluoride was prepared by reaction of Cl<sub>2</sub> with fluorine in a Monel bomb at 250 °C.<sup>10</sup> SF<sub>5</sub>OSF<sub>4</sub> was prepared by reaction of F<sub>2</sub> with SOF<sub>2</sub> at 22 °C.<sup>11</sup> Pentafluorosulfur chloride was prepared by reaction of SF<sub>4</sub> with ClF using a CsF catalyst.<sup>12</sup> Pentafluorosulfur hypochlorite was prepared by the CsF-catalyzed reaction of OSF<sub>4</sub> with ClF.<sup>13</sup> Pentafluorosulfur hypofluorite was prepared by reaction of OSF<sub>4</sub> with F<sub>2</sub> over a CsF catalyst.<sup>11,14</sup>

**Synthesis of SF<sub>5</sub>OSF<sub>5</sub>.** Pentafluorosulfur chloride (15.1 mmol) and SF<sub>5</sub>OCl (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.

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Table I

run	conditions (°C, h)	amt of SF <sub>5</sub> O <sub>2</sub> SF <sub>5</sub> (mmol)	cumulative yield (%) <sup>d</sup>
1 <sup>a</sup>	163, 22	2.61	41.4
2 <sup>b</sup>	170, 4	0.84 <sup>c</sup>	55.0
3 <sup>b</sup>	170, 17	1.49 <sup>c</sup>	78.8
4 <sup>b</sup>	170, 22	0.37 <sup>c</sup>	84.7
5 <sup>b</sup>	199, 100	0.13 <sup>c</sup>	87.0

<sup>a</sup> 6.3 mmol of SF<sub>5</sub>OF, 7.3 mmol of SOF<sub>4</sub>. <sup>b</sup> Unreacted starting materials from previous run. <sup>c</sup> Additional SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub>. <sup>d</sup> Based on starting SF<sub>5</sub>OF.

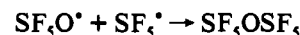
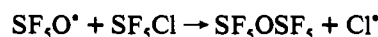
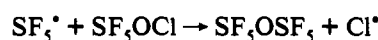
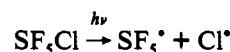
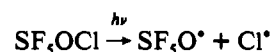
The mixture was irradiated for 4 h at 22 °C, and the reaction products were collected under dynamic vacuum in a -196 °C trap. The products were then separated by fractional condensation through traps kept at -111 and -196 °C. The -111 °C trap contained a mixture of SF<sub>5</sub>OSF<sub>5</sub> and SF<sub>5</sub>OOSF<sub>5</sub> (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<sub>5</sub>OSF<sub>5</sub>/SF<sub>5</sub>OOSF<sub>5</sub> 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<sub>5</sub>OSF<sub>5</sub> (9.2 mmol, 72% based on SF<sub>5</sub>OCl), and the -196 °C trap contained 0.3 mmol of a mixture of SO<sub>2</sub>F<sub>2</sub>, SOF<sub>4</sub>, and SF<sub>6</sub>. The properties of SF<sub>5</sub>OSF<sub>5</sub> (bp,<sup>5</sup> IR<sup>4</sup>) agreed with literature values.

**Synthesis of SF<sub>5</sub>OOSF<sub>5</sub>.** Pentafluorosulfur hypofluorite (6.3 mmol) and SOF<sub>4</sub> (7.3 mmol) were added by vacuum transfer to a 5-mL copper reactor as described above for SF<sub>5</sub>OSF<sub>5</sub>. 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<sub>5</sub>OOSF<sub>5</sub> was retained in the -112 °C trap, and unreacted starting materials along with very small amounts of SO<sub>2</sub>F<sub>2</sub> and SF<sub>6</sub> 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<sub>5</sub>OF was detectable by IR after separation of SF<sub>5</sub>OOSF<sub>5</sub>. The IR of SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> agreed with literature values.<sup>8,14</sup> The physical properties determined were slightly different from literature values: bp = 47.3 °C (49.4 °C<sup>8</sup>), mp = -93.8 °C (-95.4 °C<sup>8</sup>).

### Results and Discussion

The formation of SF<sub>5</sub>OSF<sub>5</sub> by photolysis of a mixture of SF<sub>5</sub>OCl and SF<sub>5</sub>Cl presumably results from a combination of SF<sub>5</sub><sup>•</sup> and SF<sub>5</sub>O<sup>•</sup> radicals by direct combination and by radical abstraction reactions as shown in the following simplified equations.



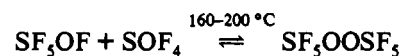
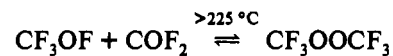
Previous results on the photolysis of SF<sub>5</sub>OCl and SF<sub>5</sub>Cl/O<sub>2</sub> indicate that SF<sub>5</sub>OSF<sub>5</sub> and SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> are formed in varying ratios depending on the reaction conditions.<sup>4,7,9</sup> In the case of SF<sub>5</sub>Cl/O<sub>2</sub>, the peroxide is the major product when it is continuously removed from the reaction mixture, whereas, in a static system, SF<sub>5</sub>OSF<sub>5</sub> is the major product. In the case of SF<sub>5</sub>OCl, the peroxide is the major product under all conditions reported, but the amount of SF<sub>5</sub>OSF<sub>5</sub> increases with irradiation time. The low yield of peroxide in this work implies an efficient radical abstraction reaction between SF<sub>5</sub>O<sup>•</sup> and SF<sub>5</sub>Cl and/or SF<sub>5</sub><sup>•</sup> and SF<sub>5</sub>OCl. The maximum yields of SF<sub>5</sub>OSF<sub>5</sub> approached 85% based on SF<sub>5</sub>OCl, making this synthesis the highest yield method by a

large margin. Increasing the ratio of SF<sub>5</sub>Cl to SF<sub>5</sub>OCl did not result in higher yields of SF<sub>5</sub>OSF<sub>5</sub>.

The removal of SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> from SF<sub>5</sub>OSF<sub>5</sub> was readily accomplished as suggested by Seppelt,<sup>5</sup> by heating the mixture to decompose the peroxide to SF<sub>6</sub>, SO<sub>2</sub>F<sub>2</sub>, SOF<sub>4</sub>, and O<sub>2</sub>, which are easily removed from the remaining SF<sub>5</sub>OSF<sub>5</sub>. A surprising result was observed in this purification process: both SF<sub>5</sub>OSF<sub>5</sub> and SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> are rapidly decomposed in a 304 stainless steel vessel above 200 °C, whereas, in copper or Monel 400, only SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> is thermolyzed. The reason for this difference in behavior is not obvious. Seppelt used a Monel vessel in preparing pure SF<sub>5</sub>OSF<sub>5</sub>.

The preparation of SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> free of SF<sub>5</sub>OSF<sub>5</sub> 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<sub>2</sub> and SF<sub>5</sub>OF.<sup>8</sup> We found that this method could be considerably improved by using SOF<sub>4</sub> in place of SOF<sub>2</sub>. Merrill and Cady had also utilized these reactants in a flow system over AgF<sub>2</sub> and Williamson and Cady<sup>2</sup> had utilized these reactants in a static system over AgF<sub>2</sub>, but the uncatalyzed reaction of SOF<sub>4</sub> and SF<sub>5</sub>OF has previously not been reported. However in reactions of SF<sub>5</sub>OF with SOF<sub>2</sub>, OSF<sub>4</sub> is surely an intermediate as suggested by Merrill and Cady.<sup>8</sup> By recycling the unreacted SOF<sub>4</sub> and SF<sub>5</sub>OF (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<sub>3</sub>OF and COF<sub>2</sub> are in equilibrium with the peroxide CF<sub>3</sub>OOCF<sub>3</sub>.<sup>16</sup>



For a given amount of starting SF<sub>5</sub>OF and SOF<sub>4</sub>, the concentration of SF<sub>5</sub>OOSF<sub>5</sub> reaches an apparent steady state at a fixed temperature, although no effort was made to examine this in detail.<sup>17</sup>

In summary, improved methods for the synthesis of pure SF<sub>5</sub>OSF<sub>5</sub> and SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> have been developed to provide standards for the analysis of the products of electrical breakdown in devices employing SF<sub>6</sub> as an insulating gas.

**Acknowledgment.** The partial support of this work by the Tobey-Beaudrot Professorship at Clemson University and the National Science Foundation is gratefully acknowledged.

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(17) A reviewer pointed out that this may be a case of a slow reaction of SF<sub>5</sub>OF with OSF<sub>4</sub> and a competing slow decomposition of SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub>. We have not shown that SF<sub>5</sub>O<sub>2</sub>SF<sub>5</sub> does indeed decompose to SF<sub>5</sub>OF and SOF<sub>4</sub>. This was beyond the scope of this work.