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PREPARATION OF PURE SULFUR TETRAFLUORIDE FOR SYNTHESIS OF ISOTOPICALLY SUBSTITUTED COMPOUNDS*

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SUMMARY

A method is described for the small-scale synthesis of SF_4 from S, Cl_2, and UF_6, which gives a product a very high purity.

INTRODUCTION

Attempts to prepare sulfur tetrafluoride date as far back as 1905 [1], but for several years workers succeeded only in making complex mixtures of uncertain composition. Then, in 1950, Silvey and Cady [2] isolated SF_4 from the products of decomposition of CF_3SF_5 by electrical discharge, and a few years later Schmidt [3] made SF_4 by heating copper turnings with the solid formed by reaction of IF_5 and S_2Br_2. Tullock, et al. [4] later showed that Schmidt's reaction proceeded at 200°C without the use of Cu, giving a yield of 88%. The same authors reported several other methods of SF_4 synthesis, utilizing SCl_2, metal fluorides (primarily NaF), and Cl_2; or S and IF_5. Although Tullock recorded substantial yields (near 100% in some cases), the amounts of impurities were large, in excess of 5-10%. Recently, Aubert, et al. [5] succeeded in making SF_4 from S and UF_6, but S_2F_2 constituted 15% of the product.

The most common impurity in SF_4 preparations is SOF_2, which is formed rapidly in the presence of traces of water. A somewhat complicated method for removal of SOF_2, involving formation of $SF_4 \cdot BF_3$ followed by heating with SeF_4 to yield $SeF_4 \cdot BF_3$ and SF_4 is described by Bartlett and Robinson [6,7]. We wished to develop a simpler method for synthesizing high purity SF_4 in reasonable yields, so that we could prepare $S^{18}OF_2$ and $^{34}S^{18}OF_2$ using SF_4 and $H_2{}^{18}O$ or $^{34}SF_4$ and $H_2{}^{18}O$. We found that SCl_2 is

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readily fluorinated by UF_6 giving a product >96% SF_4 with SOF_2 the only impurity. The reactions proceed quickly at 92°C and result in yields of 70% or better.

RESULTS AND DISCUSSION

Sulfur can be directly fluorinated with UF_6 to form SF_4, but the reaction is very slow at temperatures up to at least 130°C; it is somewhat faster if the reaction vessel is pressurized with N_2 but, even so, repeated heating with subsequent removal of product is required for quantitative yields. SCl_2 is an easily made and highly reactive intermediate, formed quickly at 92°C by mixing S and Cl_2.

$$S + Cl_2 = SCl_2 \qquad (1)$$

Any excess Cl_2 may be left in the reaction vessel during fluorination, or removed, depending on the pressure constraints of the apparatus. The reddish-orange color of the mixture formed in this step indicates the presence of S_2Cl_2 as well as SCl_2 and unreacted sulfur.

SCl_2 reacts with UF_6 according to the following equation:

$$SCl_2 + 4UF_6 = SF_4 + Cl_2 + 4UF_5 \qquad (2)$$

Excess UF_6 was condensed onto SCl_2 at liquid N_2 temperature. As the tube was warmed, white solid UF_6 began to turn light green and the volume in the tube above the solid became filled with yellow Cl_2 vapor. The progress of the reaction was monitored by observing the increase in pressure as gaseous products were formed. After constant pressure was reached, the vessel was cooled to -98°C and volatile SF_4 and Cl_2 condensed into another container where chlorine was quantitatively removed by reaction with Hg.

Analysis of the solid remaining in the reaction vessel showed unreacted S and UF_6 and a green powder which, by x-ray powder diffraction, was shown to be UF_5. Mass spectra of the gaseous product indicated SF_4 plus traces of SOF_2; absorbances at 1339 and 1329 cm^{-1} of the infrared spectrum were used to calculate the amount of SOF_2 impurity. Yields were in the range 69-78% based on S, with SOF_2 concentrations of 3.5 to 6%. There was no evidence of any gaseous species other than SF_4 and SOF_2.

Formation of extraneous thionyl fluoride was held to a minimum by treating the reaction apparatus with UF_6 which removes H_2O as follows:

$$UF_6 + H_2O = 2HF + UOF_4 \qquad (3)$$

or

$$UF_6 + 2H_2O = 4HF + UO_2F_2 \qquad (4)$$

Since sulfur does not react appreciably with UF_6 at room temperature, it was possible to treat the reaction vessel containing the starting material, as well as the remainder of the vacuum line, to rid the system of nearly all water. The line was then evacuated overnight to remove HF before proceeding with the synthesis.

EXPERIMENTAL

All reactions were carried out in a stainless steel vacuum line. Sulfur was sublimed in vacuo at 92°C. Cl_2 (Liquid Carbonic) was purified by condensing at -78°C and pumping off volatile species. UF_6 was supplied by Oak Ridge National Laboratory and was purified by trap to trap distillation with a trace of HF the only impurity remaining. Infrared spectra were recorded on a Perkin Elmer Model 180 Spectrophotometer and mass spectra were determined using a Bendix MA-2 TOF Mass Spectrometer. A standard 114.6 mm Debye-Scherrer powder camera with Cu radiation was used for powder patterns.

Approximately 1 to 2.5 mmol of sublimed S was placed in a Kel-F, Monel, or Ni reaction vessel, capacity ∿30mℓ. The bottom one inch of the tube was heated in a boiling water bath (92°C) long enough to sublime the sulfur onto the sides of the vessel, ∿1 to 2½ hr. The entire vacuum line, including all surfaces with which the product would come into contact, was treated with 50-80 torr UF_6 for several min, then evacuated overnight.

Cl_2 was condensed into the reaction vessel in quantities ∿2 x the amount of S on a mole basis, then heated at 92°C until the pressure dropped to its lowest value. A reddish-orange mixture resulted. Excess chlorine was removed by immersing the vessel in a methanol-liquid nitrogen slush bath at -98°C and evacuating.

UF_6 was condensed into the tube in quantities five to ten times the stoichiometric amount required for fluorination. The vessel was again heated at 92°C, until the pressure reached a maximum.

To remove the chlorine liberated during this step, the volatiles at -98°C (consisting of SF_4 and Cl_2) were then condensed into a dry, evacuated Monel vessel containing Hg. The tube was left at room temperature overnight to ensure complete reaction with Cl_2, though this length of time is probably unnecessary. The remaining SF_4 was analyzed for impurities by IR and mass spectrometry.

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