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SYNTHESIS OF TRIFLUOROMETHYLSULFUR PENTAFLUORIDE (CF_3SF_5)

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SYNTHESIS OF TRIFLUOROMETHYLSULFUR PENTAFLUORIDE (CF_3SF_5)

by

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1.0 Introduction

The object of this work was to prepare 100 lb. of trifluoromethylsulfur pentafluoride (CF_3SF_5), which was to be tested to determine its potential as a meteorological tracer. The gas was to be delivered in lots of 10 lb. more or less and was to meet the following quality requirements using thermal conductivity gas chromatographic analysis:

SF_6	Less than 10% of the amount of CF_3SF_5 present
SF_4	Less than 0.01% of the amount of CF_3SF_5 present
SF_2	Less than 0.01% of the amount of CF_3SF_5 present
HF	Less than 0.01% of the amount of CF_3SF_5 present
CF_4	Less than 0.01% of the amount of CF_3SF_5 present
CH_3SH	Less than 0.01% of the amount of CF_3SF_5 present
CS_2	Less than 0.01% of the amount of CF_3SF_5 present

In producing the gas every possible precaution to minimize the release of CF_3SF_5 to the atmosphere was to be made.

2.0 Summary

A quantity of 100 lb. of CF_3SF_5 was prepared by the cobalt trifluoride fluorination of bis(trifluoromethyl)disulfide (CF_3SSCF_3). It was purified by alkaline sulfite scrubbing and fractional distillation to meet the quality requirements. Precautions were taken to minimize release to the atmosphere, but about 2 lbs. were lost due to a leaking cylinder valve. Otherwise, there were no losses of any consequence.

3.0 Discussion

There were three known methods available to us at the start for the preparation of CF_3SF_5; fluorination of CS_2 or CH_3SH by cobalt trifluoride (1), by electrolytic fluorination (2), or by direct fluorination (1,3). Cobalt trifluoride is a solid which is readily entrained in a gas stream causing plugging of the reactor. It has to be regenerated by fluorine periodically. The process is generally messy and difficult to operate, and of poor yield. Electrolytic fluorination involves the use of liquid HF as the electrolyte and is extremely hazardous to work with, even more so than fluorine itself in some respects. The process is tricky to operate and control, requires cooling of the cell, and is generally a difficult process, although yields in some cases are quite high. Direct fluorination is a fairly simple straightforward gas reaction, and with a jet reactor (4,6) the yields can be quite good. Fluorine is available in cylinders and is much easier to use now than formerly, although it still requires considerabl care. Direct fluorination, therefore, appeared to be the most generally suitable method available at the start.

Methyl mercaptan, dimethyl sulfide, and carbon disulfide have all been reacted with fluorine to prepare CF_3SF_5(1,3):

$$CH_3SH + 6F_2 = CF_3SF_5 + 4HF$$
$$CH_3SCH_3 + 9F_2 = CF_3SF_5 + CF_4 + 6HF$$
$$CS_2 + 7F_2 = CF_3SF_5 + SF_6$$

Methyl mercaptan requires the least amount of fluorine. The other two require cleavage of a C-S bond, which would certainly occur in a poorly controlled reaction. In a well controlled reaction, however, such as provided by a jet reactor (4,6) less cleavage should occur and the yield of CF_3SF_5 should decrease. Under optimum conditions, therefore, methyl mercaptan should give the highest yield for a given amount of fluorine.

The reactor used in the original preparation of CF_3SF_5 was a metal packed cylinder, which gave a yield of 10% (1). Similar reactors also gave low yields of similar perfluoro-compounds (3,5,6). The jet reactor, however, has given yields of over 80% in some cases (4). Therefore, it was expected that a well controlled reaction using a jet reactor would give fairly high yields of CF_3SF_5 from methyl mercaptan.

For the above reasons, therefore, we proposed to prepare CF_3SF_5 by the direct fluorination of methyl mercaptan using a jet fluorination reactor. Such a reactor was constructed of copper tubing and readily available commercial fittings. It was tested by fluorinating propane, since we knew from previous experience that C_3F_8 could be made in high yield in this manner:

$$C_3H_8 + 8\ F_2 = C_3F_8 + 8HF.$$

Also, this reaction allowed us to check our entire reaction, scrubbing and condensing system for leaks without fear of losing any CF_3SF_5 to the atmosphere.

Accordingly, several runs were made with propane, varying flow rates, temperatures, fluorination and dilution ratios until the optimum conditions were found for preparing C_3F_8. Under these conditions C_3F_8 could be prepared in about 85% yield at about 240° at rates of about 0.7 lb./hr. The reactor, therefore, performed exactly as expected.

Next, we tried to fluorinate CH_3SH under similar conditions, but the results were completely unexpected. Whereas the C_3H_8/F_2 flame was easily blown out into a homogeneous gas phase reaction, the CH_3SH/F_2 flame could not be blown out at the highest jet velocities and dilution ratios we were

able to obtain. The yield of CF_3SF_5 was 15-20%, which is a considerable improvement over the original preparation (1) but still not enough for a practical manufacturing process. Numerous variations in the jet design and operating conditions were made, all without significant improvement in the yield. Both CS_2 and CF_3SSCF_3 were also used as starting materials, but in neither case was any significant improvement in the yield of CF_3SF_5 made. Direct fluorination, therefore, was abandoned as a preparative method, and other possible methods were investigated.

The CoF_3 preparation of CF_3SF_5 from CS_2 or CH_3SH was not attractive because the yields were still too low for a practical process (1). The reaction of CF_3SSCF_3 with CoF_3, however, was reported to give CF_3SF_5(7) and looked more promising, since 3/8 of the required fluorine was already present. Accordingly, we made a small CoF_3 reactor and tested the reaction. It was found that CF_3SF_5 was formed in about 70% yield at 100° and that by raising the temperature to 170° it could be converted to CF_3SF_5. These results were quite satisfactory, and this method, therefore, was chosen for scale up.

A conventional CoF_3 reactor of the rotating paddle wheel type was built and used to prepare CF_3SF_5:

$$CF_3SSCF_3 + 10CoF_3 = 2\ CF_3SF_5 + 10CoF_2.$$

The CF_3SSCF_3 was prepared by the NaF fluorination of CCl_3SCl in Sulfolane (8), and was fed into the CoF_3 reactor as gas. The temperature of the reactor rose from about 60° at the entrance to a maximum of about 160° near the exit. Under these conditions we were able to prepare CF_3SF_5 in 66% yield at a rate of about 1/2 lb./hr. The crude product was scrubbed with alkaline sulfite solution and condensed by dry ice. Distillation of the crude product in a low temperature

still gave pure product which met the quality requirements without difficulty. The pure CF_3SF_5 was collected in steel cylinders and shipped in increments of about 10 lb. until the required 100 lb. was prepared.

The requirement to minimize release to the atmosphere was met by installing a heated bath at the scrubber exit to degas the waste scrubber solution and by passing all waste gas streams from the reactor, gas chromatograph, traps, cylinders, etc. to a vent gas combustor where they were burned to products such as HF, SO_2 and CO_2.

4.0 Experimental

4.1 Preparation of Bis(trifluoromethyl) disulfide

CF_3SSCF_3 was prepared by fluorinating CCl_3SCl with NaF in Sulfolane following the method of Tullock & Coffman (8). CCl_3SCl (9) was added gradually to a stirred suspension of NaF in anhydrous Sulfolane, the mixture was heated gradually to about 200° over about 6 hours, and the gaseous product was collected in a dry ice cooled trap. Distillation of the crude product through a 3' X 1" ID Helipak column with a dry ice cooled head gave CF_3SSCF_3 as the major product, b. 34°, which was used without further purification in the next step. In a typical run in a 22 l. flask, 5 kg. CCl_3SCl were fluorinated to 720 gm. of the disulfide for an average yield of 27% in fair agreement with the original work (8).

It was important to maintain anhydrous conditions for this reaction. The solvent was dried over CaH_2, and the NaF was baked in an oven at 150° overnight. Even with these precautions, however, there was considerable etching of the glass apparatus, and numerous flasks and condensers were destroyed during this work.

4.2 Safety Note

Great care should be taken to avoid exposure to any of these intermediates. CCl_3SCl if very toxic (9) and is a potent lachrymator. CF_3SSCF_3 is reported to be extremely toxic as well as CF_3SCl(10) which is the major by-product of the reaction. No doubt there are other toxic materials in the reaction mixture. Particular care should be taken in disposing of the reaction residue. It is highly lachrymatory and contains many toxic materials. It should be drowned in water and flushed away as rapidly as possible.

4.3 Preparation of Trifluoromethylsulfur Pentafluoride

CF_3SF_5 was prepared by fluorinating CF_3SSCF_3 in a CoF_3 reactor of conventional design as described by Stacey & Tatlow (11). Our reactor was made of a section of steel pipe 6" ID X 40" long and held a charge of about 36 lb. CoF_3 which was stirred with steel paddles. Temperature was controlled by heating tapes and cooling coils wrapped around it and the temperature was monitored by 6 thermocouples attached to a 6-point temperature recorder. The temperature increased along the length of the reactor from about 60° at the entrance to about 160° near the exit. The CF_3SSCF_3 was fed in gas phase from a steel cylinder heated to about 60° in a water bath. The gaseous product was scrubbed with alkaline sulfite to remove HF, F_2, OF_2, SF_4, SF_2, and any other di- or tetravalent sulfur compounds. The countercurrent scrubber consisted of a 10' long section of 3" polypropylene pipe packed with 5/8" plastic pall rings and mounted vertically. Scrubber solution of 5% NaOH and 2% Na_2SO_3 was pumped from a 52 gallon polyethylene tank to the top of the scrubber and was controlled by a needle valve and rotameter. The exit liquid passed through a boiling water bath to degas it to prevent loss of CF_3SF_5 to the atmosphere, then through a phase separator to collect any high boiling products, and finally to the drain. The product gas entered through a 3/8" ID Teflon tube near the bottom and exited at the top.

The scrubbed product gas was led directly to a dry ice cooled condenser of the cold finger type, and the liquefied product was collected in a 5 l. distilling flask. After storing overnight in a dry ice chest the flask and its contents were transferred directly to the still.

The product was purified by distillation through a 3' X 1" ID Helipak column with a dry ice cooled head. The distillate was collected and packaged in steel cylinders. In a typical run, about 500 gm. of CF_3SSCF_3 was fluorinated over a period of 3 hrs. to give about 700 gm. CF_3SF_5 for an average yield of about 65%.

The CoF_3 was regenerated by passing in elemental F_2 at 150°-250°.

One difficulty which caused considerable trouble initially was the continual plugging of the scrubber inlet by dust carried over from the reactor. This was overcome by installing a 12,000 volt electrostatic dust precipitator at the reactor exit as recommended by Fowler et al (12). We agree with their statement that such a dust precipitator is a necessity for smooth operation.

4.4 Vent Gas Combustor

The combustor consisted of a shielded pre-mixed gas flame with a jet-pumped air supply. Into this air supply was fed all vent gases from the reactor, scrubber, still, gas chromatograph, etc. Any waste CF_3SF_5 from cylinders or analytical samples was also vented into this air supply. In this way all waste CF_3SF_5 had to pass through the flame front of a very hot gas flame and was burned to HF, CO_2, SO_2, etc.

4.5 Analysis of CF_3SF_5

Liquid phase samples were taken from the shipping cylinders and analyzed by gas chromatography using a 6' X 1/4" OD silica gel column at 200°. The results are summarized in the following table:

ANALYTICAL RESULTS

Shipment No.	1	2	3	4	5*	6	7	8	9	10	11
Amount, lb.	0.9	8.0	10.7	9.6	10.5	10.8	9.6	9.9	9.7	10.2	10.1
SF_6, %	0.4	1.2	0.8	0.8	-	0.9	1.3	1.0	0.6	0.8	0.9
CF_3SF_5, %	98.2	97.3	98.6	98.0	-	96.8	97.3	97.7	97.7	98.9	98.8
CF_2Cl_2, %	-	1.3	-	0.4	-	1.2	1.0	0.8	1.2	-	-
Unknown A, %	-	0.3	0.6	0.8	-	1.2	0.4	0.5	0.5	0.3	0.3
Unknown B, %	0.5	-	-	-	-	-	-	-	-	-	-
Unknown C, %	0.3	-	-	-	-	-	-	-	-	-	-
Unknown D, %	0.3	-	-	-	-	-	-	-	-	-	-
CHF_2SF_5, %	0.2	-	-	-	-	-	-	-	-	-	-

Note: Results are given as percent peak area without corrections for thermal conductivity differences.

* Sample lost.

5.0 References

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16. ABSTRACT

One hundred pounds of CF_3SF_5 were synthesized via the route:

(A) $CCl_3SCl + NaF \xrightarrow[\text{Sulfolane}]{200^\circ} CF_3SSCF_3 + NaCl$

(B) $CF_3SSCF_3 + CoF_3 \xrightarrow{170^\circ} CF_3SF_5 + CoF_2$.

Yield was approximately 27% in Step A and 65% in Step B.

Report includes experimental details of the above, together with a synopsis of results obtained with several alternate syntheses of the same product.

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