

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

## Trifluoromethylsulfur Pentafluoride

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Fluorination studies made in this Laboratory have shown that trifluoromethyl hypofluorite,  $\text{CF}_3\text{OF}$ , can be prepared by the fluorination of methanol.<sup>1</sup> It was believed that the fluorination of the sulfur analog, methyl mercaptan, might yield an analogous product. However, this was not found to be the case; instead, a compound, trifluoromethylsulfur pentafluoride,  $\text{CF}_3\text{SF}_5$ , was produced. The chemistry of this substance resembles that of sulfur hexafluoride. As work progressed, carbon disulfide was found to be superior to methyl mercaptan as a starting material because it resulted in a higher yield of trifluoromethylsulfur pentafluoride.

### Experimental

One of the fluorination procedures used was like that of Fowler, *et al.*,<sup>2</sup> who employed cobalt trifluoride as the oxidizing agent. Two reaction vessels made of flattened, four-inch copper tubing were used. These vessels contained 36 moles of cobalt trifluoride which was maintained at a temperature of  $200 \pm 10^\circ$  while methyl mercaptan vapor, diluted with nitrogen, was passed through the system. The gaseous products of the reaction were passed through a tube containing sodium fluoride, which removed hydrogen fluoride, and successively through glass traps cooled by solid carbon dioxide, and by liquid oxygen. The separation of the condensed products by fractional distillation at atmospheric pressure was complicated by the presence of a subliming solid. A crude separation of the solid and liquid in the final trap was made by filtration at the temperature of liquid oxygen. The filtrate was largely carbon tetrafluoride. The residue was refiltered at  $-120^\circ$  and in this case the filtrate was largely fluoroform. The carbon tetrafluoride and fluoroform thus obtained were further purified by fractional distillation and were identified by b. p., f. p. and gas density. The products in the first collection trap were filtered at  $-78^\circ$ . The residue from this filtration, as well as that from the previous one, was a subliming solid. Further purification of this solid was achieved by sublimation into a series of glass traps, cooled by solid carbon dioxide. This material was identified as sulfur hexafluoride. The filtrate obtained at  $-78^\circ$  was fractionally distilled in a column described by Barber<sup>3</sup> who found it to have 82 theoretical plates when operated under conditions similar to those used in this distillation. The least volatile component in this material was a colorless liquid which boiled at  $-20.4^\circ$  under 1 atm. pressure. The weight of a molar volume of the gas was  $197 \pm 1$ . The analysis of this gas, together with its density, proved its formula to be  $\text{CSF}_8$  (mol. wt. 196.07). Though no structure determination was made, the known chemistry of the elements involved led to the conclusion that the compound was trifluoromethylsulfur pentafluoride,  $\text{CF}_3\text{SF}_5$ .

The gas was analyzed for its total sulfur and fluorine content. A weighed amount of the gas was introduced into a Pyrex glass chamber containing an excess of clean metallic potassium. The resulting pressure inside the chamber was read from a manometer. The chamber was heated to a

dull redness with a gas burner until the manometer indicated that the pressure had fallen to zero. The contents of the chamber were treated with ethanol to remove the remaining potassium; then all of this material was transferred to a volumetric flask. Immediately after this operation sulfur was determined approximately by allowing an aliquot of the solution to run slowly with constant stirring into 250-300 ml. of water containing hydrochloric acid and an excess of iodine. The amount of hydrochloric acid required had been determined by titrating a sample with 6 *N* hydrochloric acid, using methyl orange as an indicator. The iodine which was not reduced by the hydrogen sulfide was titrated with standard sodium thiosulfate solution. The percentage of sulfur by weight was found to be 16.5, 16.0 and 15.8 for three determinations. The theoretical value for  $\text{CF}_3\text{SF}_5$  is 16.3%.

Fluorine was determined by titrating an aliquot of the solution obtained as described above with standard 0.1 *N* thorium nitrate solution using sodium alizarin sulfonate indicator as described by Hoskins and Ferris.<sup>4</sup> The percentage of fluorine by weight was found to be 77.3% for 12 aliquots from 4 determinations with a probable error of  $\pm 0.6\%$ . The theoretical value for  $\text{CF}_3\text{SF}_5$  is 77.5%.

In all of the reactions of this gas with potassium, a deposit of carbon was left in the residual material. The carbon was filtered off, dried and weighed. The amount of carbon thus found was approximately that which would be expected from a sample of gas containing one carbon atom per molecule.

The yield of  $\text{CF}_3\text{SF}_5$  resulting from the reaction of cobalt trifluoride and methyl mercaptan at  $200^\circ$  was about 15%, based on the quantity of mercaptan used. When the cobalt trifluoride was maintained at  $100^\circ$ , only a 5% yield of  $\text{CF}_3\text{SF}_5$  resulted. The reaction at  $250-275^\circ$  resulted in a yield of 20%. In addition to the products already mentioned resulting from the fluorination of methyl mercaptan, some of the lower sulfur fluorides were found, particularly when the preparative reaction occurred at  $100^\circ$ . Boiling point data indicated a preponderance of sulfur tetrafluoride among these fluorides; however, this compound was not obtained in the pure state by separation from the mixture of fluorination products mentioned above.

A second procedure used for the fluorination of methyl mercaptan was to pass this substance, diluted by nitrogen, into a "catalytic" reaction vessel, where it was acted upon by fluorine, also diluted by nitrogen. The apparatus with its catalyst, consisting of copper ribbon coated with fluorides of silver, and the procedure for operation were those described by Kellogg and Cady.<sup>1</sup> An excess of fluorine was used at all times. The reaction vessel was maintained at  $200 \pm 10^\circ$ . As was the case in the previous method of fluorination, a mixture of products was formed. A 10% yield of  $\text{CF}_3\text{SF}_5$  was obtained by this method. The least volatile component of the mixture of products was a colorless liquid which boiled at  $5.1^\circ$ . The density of the gas corresponded to a molecular weight of  $178 \pm 1$ . This gas was analyzed for fluorine and sulfur in a manner similar to that described above. The method differed in one respect: namely, upon heating the gas in the presence of an excess of potassium metal, the pressure did not fall to zero but rather to about one-half of the initial value. This residual gas was pumped from the combustion chamber and was found to be hydrogen. Three determinations for fluorine gave 74.6, 75.0 and 74.8%. The theoretical value for  $\text{CSHF}_7$  is 74.7%. For three determinations the percentage of sulfur by weight was found to be 17.9, 17.5 and 17.6. The theoretical value for  $\text{CSHF}_7$  is 18.0%.

(1) Kellogg and Cady, *This Journal*, **70**, 3986 (1948).

(2) R. D. Fowler, W. B. Burford III, J. M. Hamilton, Jr., K. G. Sweet, C. E. Weber, J. S. Kasper and I. Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).

(3) E. J. Barber, Doctorate Thesis, University of Washington, 1948.

(4) W. M. Hoskins and C. A. Ferris, *Ind. Eng. Chem., Anal. Ed.*, **8**, 6 (1936).

A yield of 15% of  $\text{CSHF}_7$  was obtained by the "catalytic" fluorination of methyl mercaptan at  $200 \pm 10^\circ$ . The presence of sulfuryl fluoride in the mixture of reaction products, to the extent of 35% of that theoretically obtainable from the mercaptan, may be explained as resulting from the presence of oxygen in the fluorine used in the preparative process. The sulfuryl fluoride was identified by b. p., gas density, sulfur and fluorine content.

Melting point measurements were made on  $\text{CF}_3\text{SF}_5$  and  $\text{CSHF}_7$ . The apparatus for these measurements consisted of a glass bulb 10 mm. in diameter and 30 mm. long equipped with a long, thin walled, 4 mm. tube and a micro-stopcock for filling. The bulb was centered in an aluminum shell which, in turn, was suitably supported in a double-walled vessel. This assembly was immersed in a Dewar containing the cooling medium. One single junction thermocouple was inserted in a well in the glass bulb and another was fastened directly to the aluminum shell. By suitable manipulation, a nearly linear time-temperature function could be obtained for the shell over a considerable temperature range. Transition and melting points were determined by extrapolation of the warming curves. These curves were used as a basis for estimating the heats of transition and fusion. The values so obtained may be in error by as much as  $\pm 20\%$ . A detailed description of the apparatus, as well as the procedures used for these determinations, has been given by Burger.<sup>5</sup>

For  $\text{CF}_3\text{SF}_5$ , a transition point was found at  $-153.3 \pm 0.3^\circ$ ;  $\Delta S$  for this transition was estimated to be 14 e.u. The melting point for this compound was  $-86.9 \pm 0.2^\circ$  and the  $\Delta S$  of fusion was estimated to be 2 e. u.

The observed melting point of  $\text{CSHF}_7$  was  $-87^\circ$ . The shape of the melting curve indicated a very low heat of fusion and that melting took place over a range of approximately  $2^\circ$ . Thus, it seems probable that the true melting point is slightly higher than that observed.

The vapor pressures of the two compounds were studied using apparatus described by Kellogg and Cady.<sup>1</sup> The sample of  $\text{CF}_3\text{SF}_5$  used for this purpose was a portion of the material carefully purified by the fractional distillation procedure already described. The  $\text{CSHF}_7$ , of which a limited quantity was available, was distilled in a column with packing which, like that of Mitchell and O'Gorman,<sup>6</sup> was made of continuous wire helices wound around a central Pyrex glass core. From data given in the literature<sup>6</sup> the column used in this case was estimated to operate with about 50 theoretical plates.

The relation between the vapor pressure and the absolute temperature is given by equation (a) for  $\text{CF}_3\text{SF}_5$  and by equation (b) for  $\text{CSHF}_7$ .

$$\log P_{\text{mm.}} = 6.71988 - 757.795/T - 53,771.9/T^2 \quad (\text{a})$$

The probable error in  $\log P_{\text{mm.}}$  is = 0.00023.

$$\log P_{\text{mm.}} = 6.64570 - 759.863/T - 80,107.2/T^2 \quad (\text{b})$$

The probable error in  $\log P_{\text{mm.}}$  is = 0.00040.

Table I shows a comparison of observed vapor pressures with those calculated from the equations given above. These data cover the entire range of temperatures investigated; only one-half of the experimental points (alternate temperatures) are tabulated.

The heats of vaporization were calculated using the integrated form of the Clausius-Clapeyron equation. Values of 5,380 cal./mole for  $\text{CF}_3\text{SF}_5$  and 6,100 cal./mole for  $\text{CSHF}_7$  were obtained. When the densities of the vapors and liquids of these substances are known accurately, it will, of

(5) L. I. Burger, Doctorate Thesis, University of Washington, 1948.

(6) F. N. Mitchell, Jr., and J. M. O'Gorman, *Anal. Chem.*, **20**, 315 (1948).

TABLE I  
VAPOR PRESSURES

$\text{CF}_3\text{SF}_5$			$\text{CSHF}_7$		
$T, ^\circ\text{K.}$	$P_{\text{mm.}}$ Obsd.	$P_{\text{mm.}}$ Calcd.	$T, ^\circ\text{K.}$	$P_{\text{mm.}}$ Obsd.	$P_{\text{mm.}}$ Calcd.
205.8	58.9	58.8	221.9	39.5	39.4
211.6	86.7	86.7	227.3	56.6	56.5
220.3	148.2	148.3	237.3	104.9	104.8
229.5	250.1	249.6	244.2	155.4	155.3
236.0	350.1	349.8	252.7	241.9	242.0
241.1	449.4	449.4	260.0	344.7	345.9
245.5	551.1	551.2	265.9	451.5	452.2
250.9	699.6	699.8	271.6	577.0	578.1
253.1	771.4	771.2	277.2	729.1	728.9
256.9	901.2	901.2	281.2	851.9	852.3
262.2	1113.0	1114.0	286.8	1052.0	1052.4
			292.3	1281.6	1282.0

course, be possible to calculate more precise values for the heats of vaporization.

An attempt was made to hydrolyze  $\text{CF}_3\text{SF}_5$  by allowing a sample of the gas to stand over a 6 *N* sodium hydroxide solution for 2.5 months at room temperature. At the end of this time, the gas gave no indication of change in volume or in density. Upon titration with thorium nitrate solution, no evidence for fluoride ion in the sodium hydroxide solution was found. By this method, the concentration of fluoride ion could not have been greater than 0.002 *N*.

A sample of  $\text{CSHF}_7$  was treated with 6 *N* sodium hydroxide solution in the same manner. Heat was evolved as soon as the gas was introduced into the reaction bulb. In a short time, a white precipitate was observed in the solution. An analysis showed this precipitate to be sodium fluoride; furthermore, the fluoride found as  $\text{NaF}$  and as fluoride in the hydrolysis solution accounted for all the fluorine present in the original gas sample.

Sulfur hexafluoride has been used successfully as an electrical insulating gas. Because of the inertness of  $\text{CF}_3\text{SF}_5$  and its structural similarity to sulfur hexafluoride, a series of high voltage electrical break-down measurements was made on the gas by F. S. Linn and R. Geballe.<sup>7</sup> These measurements showed  $\text{CF}_3\text{SF}_5$  to be superior to  $\text{SF}_6$  as a gaseous insulator at low pressures.

As a spark passed through the  $\text{CF}_3\text{SF}_5$ , decomposition occurred, apparently according to the reaction:  $\text{CF}_3\text{SF}_5 \rightarrow \text{CF}_4 + \text{SF}_4$ . This conclusion was reached from several observations. Sustained sparking caused the initial pressure of the gas sample to double. One of the products of decomposition was identified as carbon tetrafluoride from f. p. and gas density determinations. An attempt was made to fractionally distill the decomposition product remaining after removal of most of the more volatile carbon tetrafluoride. This was soon discontinued because of the corrosive action of the product on the metal parts of the column. Therefore, without further purification, a sample of the product was analyzed for

(7) F. S. Linn and R. Geballe, *J. Applied Phys.*, **21**, 592 (1950).

sulfur and fluorine. This gas had a density which corresponded to molecular weight 107. The theoretical molecular weight of sulfur tetrafluoride is 108. The percentage of sulfur by weight was found to be 29.2, 29.7 and 29.3 for three determinations. The theoretical value for sulfur tetrafluoride is 29.6%. The percentage of fluorine by weight was found to be 67.2 and 67.4 for two determinations. The theoretical value for SF<sub>4</sub> is 70.4%.

A sample of CSHF<sub>7</sub> was decomposed by spark-over discharge in order to learn the nature of the decomposition products. No voltage measurements were taken. Boiling point measurements made on the mixture of decomposition products indicated the presence of carbon tetrafluoride, fluoroform and sulfur tetrafluoride. A considerable amount of free sulfur was deposited on the walls of the glass reaction flask.

Carbon disulfide was allowed to react with cobalt trifluoride at 200–250° in the manner described above for methyl mercaptan. As was the case with the mercaptan, a mixture of products was obtained. A 40% yield of CF<sub>3</sub>SF<sub>5</sub> was obtained by this method. Sulfur hexafluoride and carbon tetrafluoride were the only other compounds present in sufficient quantities for separation and identification. Traces of the lower sulfur fluorides were thought to be present because of the odor of the mixture of reaction products.

**Acknowledgment.**—The authors wish to thank Drs. L. L. Burger, E. J. Barber and Mr. K. B. Kellogg for the use of apparatus constructed by

them. Gratitude is also expressed to Mr. F. S. Linn and Dr. R. Geballe for electrical breakdown measurements made on CF<sub>3</sub>SF<sub>5</sub>. This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

### Summary

Methyl mercaptan was fluorinated by cobalt trifluoride at 250° and by the action of an excess of fluorine, diluted with nitrogen, in the presence of copper turnings coated with silver fluorides, at 200°. Both methods produced trifluoromethylsulfur pentafluoride, CF<sub>3</sub>SF<sub>5</sub>, as one of the products. The second method produced what is regarded as a mono-hydrogen derivative, CSHF<sub>7</sub>. A preparative method which gave the highest yield of trifluoromethylsulfur pentafluoride was the reaction of carbon disulfide with cobalt trifluoride at approximately 250°.

Trifluoromethylsulfur pentafluoride boils at –20.4°, melts at –86.9 ± 0.2° and has a transition point at –153.3 ± 0.3°. No evidence was found for the reaction of the gas with 6 *N* sodium hydroxide at room temperature. This gas reacts rapidly with alkali metals only at dull red heat. It is a very good gaseous insulator at low pressure, but is decomposed by spark-over discharge, yielding carbon tetrafluoride and sulfur tetrafluoride.

CSHF<sub>7</sub> boils at 5.1° and melts at approximately –87°. It reacts rapidly with 6 *N* sodium hydroxide at room temperature, all the fluorine atoms being removed.

SEATTLE 5, WASH.

RECEIVED JANUARY 13, 1950

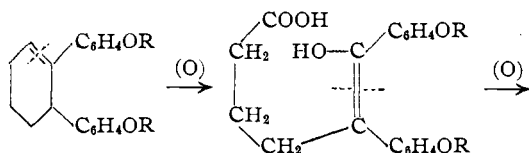
[CONTRIBUTION NO. 73 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

## 1,2- and 2,3-Bis-(*p*-methoxyphenyl)-cyclohexene

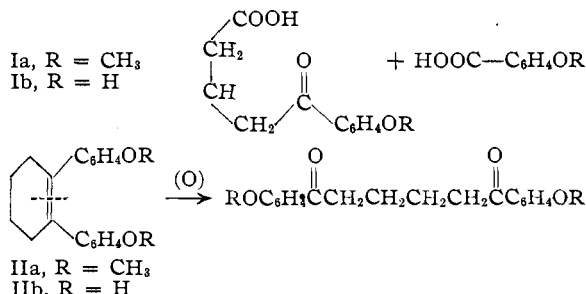
BY GEORGE P. MUELLER AND DONALD PICKENS

The reaction of *p*-methoxyphenylmagnesium bromide with either 2-chlorocyclohexanone or 2-*p*-methoxyphenylcyclohexanone followed by mild acid hydrolysis of the magnesium salts has yielded two disubstituted cyclohexenes directly. These were designated as isomers Ia and IIa in the order of their isolation and tentatively assigned the formulas 1,2- and 2,3-bis-(*p*-methoxyphenyl)-cyclohexene, respectively.<sup>1</sup> The true structures of these isomers are exactly opposite to this assignment.

Oxidation of the isomer Ia has now yielded anisic acid together with  $\gamma$ -*p*-methoxybenzoylbutyric



(1) Mueller and May, THIS JOURNAL, 71, 3313 (1949).



acid; the isomer IIa has given 1,4-bis-(*p*-methoxybenzoyl)-butane.

It seems helpful to summarize here the compounds reported in the previous paper about which any confusion could exist.

The mixture of cyclohexenes was obtained in 20% yield, of which about 95% was Ia and 3% IIa. The suggestion that alkaline demethylation of the former gave rise to IIb, in addition to Ib,