Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Short Communication

Synthesis and some properties of trifluoro(trifluoromethyl)silane

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(Received April 2nd, 1971)

The simplest perfluoroalkylfluorosilane, CF_3SiF_3, has remained essentially uncharacterized up to the present. Although a patent[1] claims synthesis from the passage of CF_3Br or C_2F_5Br over Si–Cu alloy at 400–500°, other workers have indicated that the preparation involves very low yields, or have not reported the compound from the same or closely similar reactions under comparable conditions[2–4]†. Moreover, from what is now known of the thermal stability of this class of compounds, it seems highly unlikely that CF_3SiF_3 could persist in appreciable quantities at such temperatures[4, 5].

The development of synthetic techniques based on the low-temperature reactions of the high-temperature molecule silicon difluoride has greatly expanded the potential for syntheses of perfluoro(alkylsilanes) in which the stringent conditions involved in the "direct" reactions are avoided. Thus, utilizing the recently reported[6] difluoroiodo(trifluoromethyl)silane, we have obtained CF_3SiF_3 (I) in high yields, and determined several of its salient properties.

CF_3SiF_2I was prepared from the low-temperature reaction[6] of SiF_2 with CF_3I, and was purified on a low-temperature distillation column. Reaction of gaseous CF_3SiF_2I with SbF_3, AsF_3, or AgF occurs very rapidly at 25°, and, in the case of SbF_3, proceeds at temperatures at least as low as −55°. In a typical run, 71.2 mg of CF_3SiF_2I was condensed into a bulb containing an excess of SbF_3, and the bulb contents shaken as they warmed to room temperature. The iodide was found to be completely reacted to give 36.6 mg of (I) (88%), the decomposition products C_2F_4 and SiF_4, and a small amount (*ca.* 1%) of the hydrolysis product CF_3H. Compound (I) was separated from the more volatile impurities on the low-temperature column. SiF_4, C_2F_4, and CF_3H distil from the column at −160° (5×10^{-5} torr); compound (I) distils in the range −156 to −149°.

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† Dr. F. E. Brinckman, of this laboratory, has attempted to duplicate the synthesis described in Reference 1 with the following results: No carbon- or bromine-containing volatile products except unreacted CF_3Br were observed; silicon was recovered as the mixed fluorochloromonosilanes. The source of the chlorine is the cuprous chloride used to prepare the Si–Cu alloy. (Private communication.)

The ^{19}F NMR spectrum of (I) in a 50% solution in CF_3I consists of two identical quartets [J(F–F) = 10.9 Hz] at 66.3 [CF_3] and 150.7 [SiF_3] ppm*. From the ^{29}Si satellite spectra, J(Si–F) = 273.2 Hz and J(Si–C–F) = 72.2 Hz. The magnitude of the Si–F coupling constant for the directly-bonded nuclei is larger than might be anticipated from the relationship of J(Si–F) and substituent electronegativities for SiF_3X compounds; it is quite close to that observed (267.2 Hz) in CH_3SiF_3[7].

The mass spectrum of (I) was obtained using a 180 degree sector, magnetic deflection instrument and was found to be related to those of Si_2F_6[8] and C_2F_6[9], in that the molecular ion $CSiF_6^+$ is of negligible intensity at electron voltages down to at least 17 eV. The most intense ion at 70 eV is $CSiF_5^+$, followed by SiF_3^+, CF^+, CF_2^+, CF_3^+, SiF^+, SiF_2^+, $CSiF_4^+$ (very small). The placement of SiF_3^+ and CF_2^+ in the preceding sequence is somewhat uncertain because of the presence of SiF_4 and C_2F_4 as thermal decomposition products in the ion source of the mass spectrometer. At 17 eV, the CF_2^+ ion is at least an order of magnitude more intense than any other.

The infrared spectrum of (I) from 2000–200 cm^{-1} has been determined. Frequencies and relative intensities are as follows: 1251 (w), 1133 (vs), 1023 (s), 866 (m), 730 (vw), 520 (vw), 495 (m), 354 (m), 261 (w). By analogy with C_2F_6, Si_2F_6, and other molecules containing a CF_3 or SiF_3 function, one may assign the two highest frequency bands to antisymmetric and symmetric C–F stretching vibrations, respectively; the next two bands to antisymmetric and symmetric Si–F stretches. The two strongest remaining absorptions, at 495 and 354 cm^{-1}, are most probably due to CF_3 and SiF_3 deformations.

A preliminary investigation of the microwave spectrum of (I) has been undertaken. Results to date are completely consistent with the assignment of CF_3SiF_3 as the structure of (I)[10].

The molecular weight of (I) was determined by the Dumas method (calcd., 154.1; found, 154.6).

Basic hydrolysis of (I) with excess aqueous NaOH yields CF_3H as the only volatile product. Vapor phase hydrolysis with a deficiency of water vapor gives CF_3H and SiF_4, but no volatile oxygen-containing species.

The thermal stability of (I) is of interest in view of the results of other workers on highly halogenated organosilanes:

$$CCl_3SiF_3 \xrightarrow{140^\circ\text{–}180^\circ} :CCl_2 + SiF_3Cl \qquad \text{(Ref. 11)}$$

$$CF_2HCF_2SiF_3 \xrightarrow{150^\circ} CF_2H\ddot{C}F + SiF_4 \qquad \text{(Ref. 12)}$$

Quantitative decomposition of (I) is observed at temperatures as low as 78° (17 h), and decomposition proceeds rapidly at temperatures above 100°. In all

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* Reported relative to external $CFCl_3$, using the relationship $\delta(CF_3I\text{–}CFCl_3) = 4.78$ ppm.

instances the products are SiF_4, C_2F_4, and cyclo-C_3F_6. The typical amount of C_2F_4 recovered represents 90% of the carbon-containing products. If one makes the reasonable assumption that CF_2 is the source of C_2F_4, the pyrolysis of (I) apparently represents the most labile vapor phase thermal source of CF_2 yet reported. Investigations of the reaction chemistry of (I), both as a source of difluorocarbene and as a derivative of SiF_4, are currently underway. Other work in progress includes synthesis of $C_2F_5SiF_3$ from its iodosilane analog.

The authors wish to express their appreciation to Drs. R. B. Johannesen and B. Coxon for assistance with the NMR spectra.

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