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Silicon-Substituted Derivatives of Trifluoro(trifluoromethyl)silane. Some Chemistry of the Silicon–Iodine Bond in a Polyhalo System

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The fluoroiodosilane CF_3SiF_2I has been utilized to generate a series of compounds of formula CF_3SiF_2X, where X = Br, Cl, F, and $OSiF_2CF_3$; all but X = F are new compounds. Conversion of Si–I bonds to Si–X is effected by antimony(III) halides or, for oxygen, mercury(II) oxide. Each of the halodifluoro(trifluoromethyl)silanes undergoes pyrolytic decomposition at 100° to generate SiF_3X and CF_2, although the thermal decomposition of CF_3SiF_2I is quite complex. Each of the CF_3SiF_2X species (other than CF_3SiF_3) reacts with water vapor to generate CF_3SiF_3 and, for X = Br or I, CF_2HX. The halodifluoromethanes evidently result from the reaction of CF_2 with HX—the CF_2 in turn resulting from the interaction of water vapor and CF_3SiF_3 at room temperature. Correlations of fluorine chemical shifts and directly bonded silicon–fluorine coupling constants between CF_3SiF_2X species and the corresponding SiF_3X species are presented.

Introduction

The known chemistry of the silicon–iodine bond in polyhalo systems is quite limited. Trichloroiodosilane has been described, but its known reaction chemistry consists of a single reaction.[1] Trifluoroiodosilane remains a rather elusive molecule; several synthetic routes to SiF_3I have been described,[2-4] but no definitive evidence for isolation of the pure compound exists, and its chemical properties remain unknown, except for a purported susceptibility toward redistribution at 700°.[2] The absence of a well-characterized reaction chemistry for SiF_3I is particularly unfortunate in view of the extensive use of CF_3I both in generating trifluoromethyl derivatives of main group elements and as a convenient homolytic source of the trifluoromethyl radical.[5]

An attractive feature of the silicon–iodine bond apparent in the chemistry of iodosilane and iodotrimethylsilane is its ability to serve as the basis for a "conversion series" whereby iodine can be selectively exchanged for a variety of halo or pseudohalo functions via silver[6] or mercury(II)[7] halides or pseudohalides. The extension of such a series to Si–I bonds in polyhalo systems has not yet been established, nor has a wide range of halogenating agents been explored.

The synthesis of difluoroiodo(trifluoromethyl)silane, CF_3SiF_2I,[8] has provided a polyhalosilane (or perhalo if the CF_3 group is accorded a pseudohalogen status) containing a Si–I bond whose accessibility and stability permit the systematic development of its reaction chemistry. This compound has recently been utilized in the first synthesis of CF_3SiF_3,[9,10] the simplest perfluoro(alkylsilane). The chemical and physical properties of several new derivatives of CF_3SiF_3—of general formula CF_3SiF_2X—will be discussed in the following sections.

Experimental Section

All volatile materials were manipulated in a grease-free vacuum system constructed of borosilicate glass, fluorocarbon polymer stopcocks, and glass "O" ring connectors. Solids were handled in an inert-atmosphere glove box. Reagents were obtained from commercial sources and, subsequent to purity verification, were used as received. Molecular weights were calculated from vapor density measurements (Dumas method). Infrared spectra were taken on a commercial double-grating instrument (Beckman IR-20A) in the range 4000–350 cm^{-1}. ^{19}F NMR spectra were run on a Varian T-60 (56.4 MHz).

Synthesis of CF_3SiF_2I. Difluoroiodo(trifluoromethyl)silane was synthesized from the low-temperature reaction of silicon difluoride with trifluoroiodomethane, as previously described.[8] Although the reaction of SiF_2 with CF_3I has been shown to be quite complex, use of a moderate excess of CF_3I in the reaction mixture allows recovery of the desired product in up to 40% overall yield, based on estimated SiF_2 production.

Reactions of CF_3SiF_2I with SbX_3. "Conversion" reactions were conducted by distilling the CF_3SiF_2I into a bulb containing an excess of the antimony halide and, for X = Cl, $SbCl_5$, isolating the bulb from the vacuum system and shaking the contents of the bulb as they warmed from liquid nitrogen temperature. Color changes indicative of reaction occurred in the solid well below room temperature in the fluoride and chloride systems. For the synthesis of CF_3SiF_2Cl, the following data correspond to a representative reaction. A 0.93-mmol sample of CF_3SiF_2I was distilled into a bulb containing 29.6 g (130 mmol) of $SbCl_3$ and 0.97 g (3.2 mmol) of $SbCl_5$. The reaction produced 0.47 mmol of CF_3SiF_2Cl (51% theoretical yield), with the remainder of the products consisting of approximately equal quantities of CF_3SiF_3 and $(CF_3SiF_2)_2O$, along with a much smaller amount of unreacted CF_3SiF_2I. The source of the oxygen is either water in the "anhydrous" $SbCl_3$ or Sb–O bonds in the solid, or both. Yields for the system where X = Br were somewhat lower than for X = Cl; yields for the production of CF_3SiF_3 were considerably higher, often surpassing 90%.

Purification of the compounds described in this work was effected by either simple trap-to-trap or low-temperature column distillation. Molecular weights for CF_3SiF_2X, where X = F, Cl, Br, I: calcd, 154.1, 170.5, 215.0, 262.0; found, 154.6, 170.5, 216.5, 260.8.

Reaction of CF_3SiF_2I with HgO, Sb_2O_3, and Ag_2CO_3. Several oxygen-containing compounds were employed in attempts to convert the Si–I function in CF_3SiF_2I into a siloxane (i.e., $CF_3SiF_2OSiF_2CF_3$). CF_3SiF_2I reacts rapidly with antimony(III) oxide at or below room temperature, but $(CF_3SiF_2)_2O$ could not be isolated among the products. Instead, SiF_4, C_2F_4, and CF_3SiF_3 are generated in substantial quantities, along with smaller amounts of SiF_3OSiF_3. Silver carbonate has been utilized in conversion of a P–I bond into a diphosphoxane containing a P–O–P linkage;[11] however, interaction of CF_3SiF_2I with Ag_2CO_3 led to formation of CF_3SiF_3 in the presence or absence of added $SbCl_5$.

Mercury(II) oxide did prove to be effective in the generation of the desired siloxane if small amounts of $SbCl_5$ were present. In a typical run, 2.81 mmol of CF_3SiF_2I was distilled into a bulb containing 26 g (120 mmol) of HgO and 1.0 g (3.3 mmol) of $SbCl_5$. The bulb was allowed to warm to room temperature and the bulb contents were shaken for 5 min. The reaction generated 0.53 mmol of $CF_3SiF_2OSiF_2CF_3$ (38% theoretical yield), with the balance of the products being largely CF_3SiF_3. Smaller amounts of CF_3SiF_2Cl (from the apparent activity of $SbCl_5$ as a chlorinating agent) and unreacted starting material were also present. Longer contact times of CF_3SiF_2I

with the solid resulted in partial conversion of $(CF_3SiF_2)_2O$ to CF_3SiF_3.

Attempted Reaction of CF_3SiF_2I with Mercury. The interaction of CF_3SiF_2I with mercury was examined in the hope of obtaining a Wurtz-type reduction of the silane to yield $CF_3SiF_2SiF_2CF_3$. In a sealed tube containing a large droplet of mercury and CF_3SiF_2I at a pressure of 100 Torr, no evidence of reaction was obtained after 20 hr at 25° in the dark. The bulb was continuously shaken during the experiment.

Hydrolytic Reactions. Vapor-phase hydrolytic reactions of the CF_3SiF_2X species were examined in such a way that system composition could be monitored as a function of time by means of infrared spectroscopy. Details for the CF_3SiF_2I–water vapor system are given below.

CF_3SiF_2I–Water Vapor. The system $CF_3SiF_2I–H_2O$ was studied as follows. Reactants were enclosed in the two compartments of a gas-mixing cell in tandem with a gas infrared cell. Small amounts of water vapor were added sequentially to pure CF_3SiF_2I and the resultant system monitored via its infrared spectrum. A deficiency of water vapor in the range 10:1 to 2:1 initially yields two products: CF_3SiF_3 and a smaller amount of a material with a strong, broad absorption at 1180 cm^{-1}, characteristic of an Si–O–Si stretch in a fluorosiloxane.[12] On standing for 60 min, a sample of composition 2.5:1 showed extensive further decomposition of CF_3SiF_2I but no significant increase in the amounts of the two compounds cited above. Silicon tetrafluoride was then present, and a white involatile polymer was apparent on the walls of the apparatus. Creation of heterogeneous conditions by condensing the volatiles in the cold finger of the cell and revaporizing several times facilitated the decomposition. After six such cycles, the above sample (2.5:1 silane to water) contained no detectable starting material. The amounts of CF_3SiF_3 and SiF_4 had increased, but the siloxane had begun to recede. Further degradation of the system by adding more water (to a ratio of 1.9:1) occurred by (1) disappearance of the siloxane, (2) attack of the CF_3SiF_3 to form its known hydrolysis products CF_3H and SiF_4, and (3) formation of a new compound with major infrared bands at 1093, 1084, and 635 cm^{-1}.

The latter compound was shown to be difluoroiodomethane via comparison with an authentic sample of CF_2HI prepared from the reaction of CF_2 with HI. The source of the CF_2 in the latter reaction was the pyrolytic decomposition of CF_3SiF_3 at 100°.[9]

Pyrolytic Reactions. Thermal decomposition processes were examined by distilling samples into well-flamed glass ampoules of approximately 50-ml volume. The ampoules were sealed and heated to 100°. Subsequent to heating the vessels were mechanically broken while attached to the vacuum line.

CF_3SiF_2X, X = F, Cl, Br. Each of these compounds decomposes rather rapidly in the vapor phase at 100° (with half-lives less than 30 min) to a mixture of C_2F_4, c-C_3F_6, and SiF_3X. Neither of the mixed halosilanes, SiF_3Cl or SiF_3Br, was observed to react with CF_2 or to undergo reactions involving redistribution of halogens under these conditions.

CF_3SiF_2I. The vapor-phase decomposition of CF_3SiF_2I is considerably more complex than those of the other halodifluoro(trifluoromethyl)silanes. Pyrolysis of a sample at 250 Torr and 100° proceeds with a half-life of starting material of ca. 12 min to give products in all three phases on cooling to room temperature. If the pyrolysis is terminated before destruction of the starting material is complete, the colors of the solid products range from orange to brick red; two liquid products of low volatility but relatively high mobility were ruby red and yellow, respectively. Gaseous products of the pyrolysis were identified by infrared and/or NMR spectra as (in approximate order of decreasing abundance) unreacted CF_3SiF_2I, CF_3SiF_3, Si_2F_6, SiF_3I, and CF_2I_2. At least two further, presently uncharacterized compounds were also present in the volatile fraction. It is noteworthy that little or no tetrafluoroethylene is generated under conditions of incomplete pyrolysis.

Extension of the pyrolysis to conditions of total destruction of CF_3SiF_2I results in considerable deposition of colored solids and the yellow liquid discussed above and a somewhat different spectrum of volatile products as well. Most notably, C_2F_4 and SiF_4—the thermal decomposition products of CF_3SiF_3—are now abundant.

Results and Discussion

The fluoroiodosilane CF_3SiF_2I has been found to be a convenient source of several new species of general formula CF_3SiF_2X. These compounds are air-sensitive gases (for X = F, Cl, or Br) or liquids (X = OCF_2SiF_3), stable at room temperature in the vapor phase[13] but susceptible to pyrolytic or hydrolytic decomposition. The compounds in this series may be legitimately viewed as derivatives of CF_3SiF_3, the simplest perfluoro(alkylsilane), or of the appropriate SiF_3X species on substitution of a CF_3 group for F. The following sections will describe synthetic routes to, characterization of, and pyrolytic and hydrolytic reaction chemistry of these halodifluoro(trifluoromethyl)silanes.

Table I. Infrared Spectral Frequencies for Halodifluoro(trifluoromethyl)silanes $CF_3SiF_2X^a$

X = I: 1232 s, 1127 vs, 989 m, 896 s, 742 w, 539 m, 505 m, 403 m
X = Br: 1234 m, 1128 vs, 997 s, 906 s, 740 w, 558 s, 520 w, 410 m
X = Cl: 1245 m, 1132 vs, 1007 s, 919 s, 748 w, 624 s, 443 m
X = $OSiF_2CF_3$: 1269 m, 1224 m, 1180 vs, 1129 vs, 1015 s, 952 m, 903 m, 671 w, 507 m
X = F: 1251 w, 1133 vs, 1023 s, 866 m, 730 vw, 520 vw, 495 m, 354 m

[a] Frequencies in cm^{-1}. Intensities: s, strong; m, medium; w, weak; v, very.

Synthetic Routes to CF_3SiF_2X. The selective exchange of halo or pseudohalo groups between silicon and silver[6] or mercury(II)[7] salts has proved to be a versatile and highly useful synthetic technique. An example of such a reaction is

$$2SiH_3Br + Ag_2O \rightarrow SiH_3OSiH_3 + 2AgBr$$

Such reactions are apparently irreversible, and one may construct "conversion series" of the type I → S → Br → Cl, CN → O → F to indicate the direction of allowed exchange on silicon. The silanes used to establish these series were either simple halosilanes or halotrimethylsilanes. We report here the extension of such exchange reactions to polyhalo (or perhalo if CF_3 is considered to be a pseudohalo function) systems and the utility of antimony(III) halides as halogenating agents.

Antimony(III) fluoride has proved useful as a "soft" fluorinating agent for both metal–[14] and nonmetal–halogen[15] bonds. We find that SbX_3 reacts smoothly with CF_3SiF_2I to generate CF_3SiF_2X where X = F, Cl, or Br. As expected from consideration of the appropriate bond and lattice energies, the efficiency of the reactions decreases in the order F > Cl > Br. Although Sb_2O_3 is ineffective in synthesizing the siloxane $(CF_3SiF_2)_2O$, the latter is accessible through reaction of CF_3SiF_2I with HgO in the presence of small amounts of antimony(V) chloride.

Both AgCN and $Hg(CN)_2$ were employed in attempts to synthesize CF_3SiF_2CN. The latter would be a potential source of the elusive molecule SiF_3CN. In neither system was exchange observed. Silver cyanide caused decomposition of CF_3SiF_2I into CF_3SiF_3, C_2F_4, and SiF_4; interaction of the silane with mercury(II) cyanide produced only small amounts of CF_3SiF_3.

Attempts to reduce the Si–I bond in CF_3SiF_2I with mercury at room temperature were unsuccessful.

Spectroscopic Characterizations. In addition to vapor density molecular weights (see Experimental Section) and chemical behavior, the compounds described here were characterized largely on the basis of their infrared and fluorine NMR spectra.

The infrared spectra of species of interest are presented in Table I. The spectra contain the characteristic stretching frequencies of Si–F, Si–Cl, Si–Br, Si–I, and Si–O bonds in the appropriate molecules. The most notable feature in the spectra is the remarkable insensitivity of the asymmetric group stretch of the CF_3 group (near 1130 cm^{-1}) to the nature of the group X on silicon. The higher of the stretching frequencies associated with the SiF_2X group (near 1000 cm^{-1}) decreases

Table II. Fluorine NMR Spectral Parameters for Halodifluoro(trifluoromethyl)silanes

	δ_{CF_3}[a]	δ_{SiF_2X}	$\lvert J_{FF}\rvert$[b]	J_{SiF}[b,c]
CF_3SiF_2I	69.9	120.1	6.9	342.4
CF_3SiF_2Br	68.3	127.8	8.2	321.7
CF_3SiF_2Cl	67.9	134.3	8.9	303.7
CF_3SiF_3	66.3	150.7	11.0	273.2
$(CF_3SiF_2)_2O$	66.9	148.7	10.9	270.9

[a] Chemical shifts in ppm upfield from CCl_3F. Values for CF_3SiF_2I are for a neat sample referenced to external CCl_3F; values for the other compounds in the table correspond to samples including some CF_3SiF_2I, which was used as an internal reference. [b] In Hz. [c] We assume, following the findings of Johannesen et al.[16] that J_{SiF} is always >0.

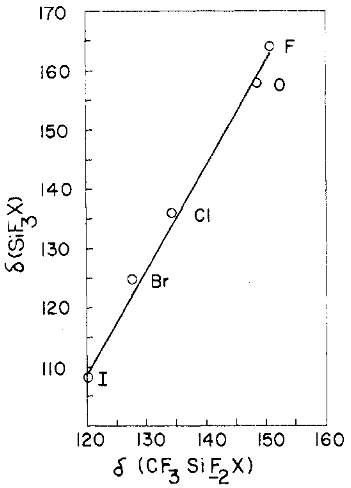

Figure 1. Correlation of chemical shifts for fluorines in halotrifluorosilanes with those of silicon-bonded fluorines in halodifluoro(trifluoromethyl)silanes. Values are in ppm upfield from CCl_3F. The value for SiF_3I is an average of the values reported in ref 4 and 8.

smoothly in the order F > O > Cl > Br > I.

The frequency of the Si–O–Si stretch in the siloxane $(CF_3SiF_2)_2O$ is similar to that in $(SiF_2Cl)_2O$[12] and lower than that in $(SiF_3)_2O$.[12] The latter finding is rather surprising, since one might expect the ability of the CF_3 group to serve as a strong σ acceptor but weak π donor to enhance the π component of the Si–O bond and hence increase its stretching frequency.

Fluorine NMR spectral parameters are listed in Table II. All spectra are first order due to the large difference in chemical shifts between the C–F and Si–F resonances. If the series of compounds is considered in the order I → Br → Cl → O, F, three correlations are evident from the NMR spectra: (a) $|J_{FF}|$ increases; (b) δ_{SiF_2X} increases; (c) J_{SiF} decreases. There are some reversals in order between O and F, but in all instances the differences between parameter values for O and F functions are small.

Correlations between $|J_{FF}|$ and substituent electronegativities in fluoroethanes have been developed[17,18] but are *opposite* in direction to those reported here. The chemical shift of the CF_3 group is relatively insensitive to the nature of X but increases monotonically in the order F < O < Cl < Br < I. The progression to higher field for the fluorines in the SiF_2X function as X changes from I through F is consistent with the trend observed in the analogous SiF_3X species. Figure 1 demonstrates the very nearly linear relationship between δ_{SiF_3X} and $\delta_{CF_3SiF_2X}$ as a function of X. J_{SiF} is quite sensitive to the nature of X and should also prove to be of diagnostic value in systems such as these. Figure 2 is a plot of J_{SiF} in SiF_3X vs. J_{SiF} in the corresponding CF_3SiF_2X. The figure clearly reveals the close correlation between the variation of the directly bonded Si–F coupling with substituent in the two systems. The behavior of J_{SiF} as a function of substituents on silicon has been discussed in detail elsewhere.[16]

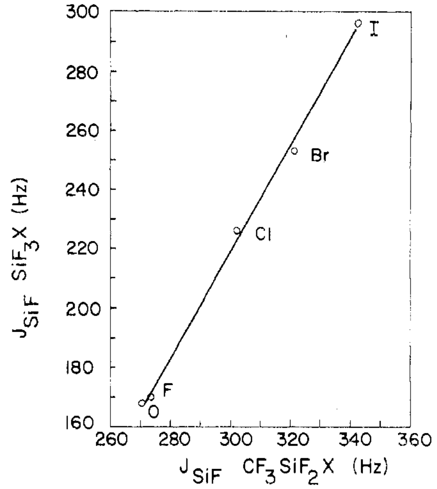

Figure 2. Correlation of directly bonded Si–F coupling constants for halotrifluorosilanes with those for halodifluoro(trifluoromethyl)silanes.

Pyrolytic Decompositions. CF_3SiF_2X, X = F, Cl, Br. The disparity of approximately 20 kcal/mol between the Si–F and C–F bond energies provides the basis for the thermal decomposition of CF_3SiF_3 into $CF_2 + SiF_4$ under mild conditions (≤100°).[9] We find that CF_3SiF_2Cl and CF_3SiF_2Br behave similarly; that is, each is thermally decomposed rapidly above 100° to form C_2F_4 and c-C_3F_6 (the products derived from CF_2 in the absence of effective trapping reagents) and SiF_3Cl and SiF_3Br, respectively. Surprisingly little has been reported on the chemistry of these halotrifluorosilanes; we feel that the processes just described represent the most straightforward specific synthetic routes to these species.

CF_3SiF_2I. The vapor-phase pyrolysis of CF_3SiF_2I appeared to be an ideal route to the little-known compound SiF_3I—the silicon analog of the enormously useful CF_3I. Although SiF_3I is generated in the pyrolysis of CF_3SiF_2I, the thermolytic process is substantially more complex than those of the other CF_3SiF_2X species discussed above. Partial or total thermal destruction of the starting material at 100° generates, after cooling to 25°, a multitude of products in vapor, liquid, and solid phases. The more volatile portion of the products includes CF_3SiF_3, SiF_3I, Si_2F_6, CF_2I_2, C_2F_4, and SiF_4. Condensed-phase products include several highly colored solids and low-volatility (but highly mobile) liquids. Several new—as yet uncharacterized—species are present as reaction products, and product composition is a function of the extent to which decomposition is carried. This is clearly a system of considerable complexity, and elucidation of the mechanism(s) of decomposition must await further efforts, perhaps involving pyrolysis of CF_3SiF_2I in the condensed phase where continual system monitoring via NMR is possible. Our present assumption is that the decomposition process is being complicated by either homolytic cleavage of the Si–I bond or interaction of CF_2 with Si–I bonds (and I_2, if present), or both.

Hydrolytic Decomposition. What little is known about the hydrolytic behavior of fluorosilanes results almost exclusively from studies in condensed media.[19] We have discovered that several fluorosilanes are surprisingly resistant to hydrolytic decomposition when exposed to limited amounts of water vapor under homogeneous conditions. Our interest in hydrolytic processes in this work was stimulated by a puzzling observation of CF_3SiF_3 as a persistent side product in reactions of CF_3SiF_2I with various of the solid reagents utilized in the conversion series. The suspicion that small amounts of water retained by the solids might be responsible for the behavior was justified by the investigation of the reaction of CF_3SiF_2I with water vapor. Mixing of the two vapors was effected in a gas-mixing cell in which one compartment was a gas infrared cell. Infrared spectroscopic monitoring of the system revealed initial formation of CF_3SiF_3 and a compound with a strong absorption at 1180 cm^{-1}, a frequency typical of Si–O–Si stretches in fluorosiloxanes. Although not observable in the infrared spectra, HI is also initially present. Admission of additional water vapor and/or subjection of the reactants to quench–vaporize cycles result in, sequentially, (1) depletion (and finally consumption) of the CF_3SiF_2I, (2) loss of the siloxane, and (3) appearance of the known hydrolytic products of CF_3SiF_3—CF_3H and SiF_4—and formation of CF_2HI.

The presence of HI in the system strongly suggests hydrolytic attack of the silicon–iodine bond to give a silanol, which rapidly condenses to a siloxane

$$CF_3SiF_2I + H_2O \rightarrow HI + CF_3SiF_2OH$$

$$2CF_3SiF_2OH \rightarrow CF_3SiF_2OSiF_2CF_3 + H_2O$$

The identity of the siloxane was verified by its independent synthesis from the reaction of CF_3SiF_2I with HgO (see Experimental Section for details). The siloxane itself is attacked by water vapor—somewhat less rapidly than the starting material—to give CF_3SiF_3 and involatile polymeric materials.

An important related experiment is the determination of the source of difluorocarbene responsible for the formation of CF_2HI (HI is one of the few efficient room-temperature traps for CF_2). The facts that CF_2HI is not observed so long as CF_3SiF_2I remains in the system and that SiF_3I is not observed among the products suggest that CF_3SiF_3 may be the source of the CF_2. In a control experiment, CF_3SiF_3 in the presence of excess HI was exposed to water vapor under conditions similar to those described above for the hydrolysis of CF_3SiF_2I. CF_2HI is indeed formed under these conditions, along with SiF_4. Anhydrous HI alone does not affect CF_3SiF_3.

CF_3SiF_2Cl and CF_3SiF_2Br behave similarly to CF_3SiF_2I on exposure to water vapor. Each suffers hydrolytic attack on the heavier halogen and generates CF_3SiF_3 through the intermediate siloxane $(CF_3SiF_2)_2O$. A secondary reaction of CF_2 with HBr leads to CF_2HBr; however, reaction of CF_2 with HCl at 25° is apparently too slow to suppress effectively the dimerization of the carbene to C_2F_4.

In summary, the hydrolytic reactions suggest the rate of attack of water vapor on Si–X bonds follows the order $I > Br > Cl$, $O > F$. When only Si–F bonds are present—in CF_3SiF_3—the Si–F bond is apparently not directly attacked.[20] Instead, water vapor, perhaps acting through an intermediate acid–base complex, promotes α transfer of fluorine to form SiF_4 (again, perhaps complexed) and CF_2. In the presence of the unusually good halocarbene traps HBr and HI the difluorocarbene can be trapped as CF_2HX.

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Registry No. CF_3SiF_2I, 27668-68-4; CF_3SiF_2Br, 54484-28-5; CF_3SiF_2Cl, 54484-29-6; CF_3SiF_3, 335-06-8; $(CF_3SiF_2)_2O$, 54484-30-9; $SbCl_3$, 10025-91-9; $SbCl_5$, 7647-18-9; HgO, 21908-53-2.

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(20) Evidence to support this claim arises from the fact that $CF_3SiF_2OSiF_2CF_3$ is not observed in CF_3SiF_3–H_2O vapor systems.

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Kinetics and Mechanism of Carborane Formation

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The kinetics of 1,2-dicarba-*closo*-dodecaborane(12) formation from $B_{10}H_{12}[(CH_3)_2S]_2$ and several acetylenes [$HC{\equiv}CCH_2Br$, $HC{\equiv}CCH_2OC({=}O)CH_3$, $HC{\equiv}C(CH_2)_2CH_3$, $HC{\equiv}C(CH_2)_5CH_3$, $HC{\equiv}C(CH_2)_3Cl$] have been studied. A mechanism is proposed consistent with the data obtained. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ correlate well with the Taft polar substituent constants for the acetylene substituents.

A wide variety of substituted 1,2-dicarba-*closo*-dodecaborane(12) derivatives have been synthesized and characterized.[2-4] The most common method for their preparation is through the use of diligand derivatives of decaborane, $B_{10}H_{12}L_2$ (L = Lewis base), and acetylenes. Alkyl derivatives are generally prepared in low yields, ca. 30–40%, from the corresponding acetylenes while other derivatives from acetate and halogen-containing acetylenes are prepared in higher yields (ca. 80–90%).

Except for some preliminary work carried out by the authors at the Rohm and Haas Redstone Research Laboratories in the middle and late 1960's, very little attention has been given to the kinetics of carborane formation. Our preliminary studies indicated that the reaction was first order in $B_{10}H_{12}L_2$ and