Chemistry of Silicon Difluoride

This high-temperature molecule has revealed unique approaches to the synthesis of novel silicon compounds.

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Species containing metals or metalloids in a state of low oxidation may be conveniently formed by the reduction of more highly oxidized species with the element itself. Such reactions may produce stable compounds in a low state of oxidation or, in a number of cases, species which are unstable and reactive, whose reactions lead to new and interesting chemistry. Such unstable, reactive molecules have often been prepared at high temperatures and then quenched to low temperatures so that chemical and physical properties might be investigated.

Studies on reduced species containing silicon and fluorine were initiated by Pease (*1, 2*) and by Schmeisser and Ehlers (*3*). In their early reports they describe the formation of polymers, presumably of silicon difluoride (SiF_2), by analogy with the carbon-fluorine system and also copolymers of this substance with other materials (*1*). The existence of SiF_2 monomer was inferred by the preparation of dichlorodifluorosilane (SiF_2Cl_2), and other difluorosilane derivatives, and by the fact that the polymer was formed only at fairly low temperatures. About this same time, some emission spectra from discharges through silicon tetrafluoride (SiF_4) were obtained and assigned to the species SiF_2 (*4*).

Since that time, many chemical and physical characteristics of the Si–SiF_4 system have been studied. The nature of the species produced when SiF_4 or calcium fluoride (CaF_2) react with hot silicon has been investigated by transpiration experiments (*5*), and by mass spectrometry (*6, 7*). From the CaF_2 + Si reaction, the standard heats of formation ($\Delta H^0_{f,\,928}$) for SiF(gas) and SiF_2(gas) were reliably established as -3 ± 5 and -139 ± 4 kilocalories per mole, respectively. The evidence indicated that by far the most abundant species formed in the Si–SiF_4 reaction was SiF_2; no SiF_3 could be detected, and there was very little evidence for the reaction:

$$SiF_2 + SiF_4 \rightarrow Si_2F_6.$$

Most of the preparations of SiF_2 have been at about 1150°C (*7*) and at this temperature there is approximately a 1 : 1 mixture of SiF_2 and SiF_4. At higher temperatures a greater proportion of SiF_2 is obtained; at 1400°C, up to 90 percent of SiF_2 can be found (*8*).

Silicon difluoride (gas) is fairly unreactive at room temperature, but below -70°C it polymerizes irreversibly, the result being the polymer first described by Pease (*1*), together with small quantities of perfluorosilanes (*7*). The rate of disappearance of monomeric SiF_2 (gas) was measured with a Bendix time-of-flight mass spectrometer, and a half-life for the species of about 150 seconds was obtained (*7*). This value is greatly in excess of the half lives reported for other carbenes (*9*), and is not greatly affected by the addition of other gases, some of which were later shown to react with SiF_2 in condensed phases (*10*).

The long half-life of SiF_2(gas) has permitted measurements to be made, of the microwave spectrum (*11*) and of the ultraviolet absorption spectrum (*12*) (Table 1 and Fig. 1).

Silicon difluoride appears to be fairly unreactive chemically in the gas phase, but many chemical reactions can be performed by cocondensation of the species with a particular reactant. These facts, and the nature of the products formed in the cocondensation reactions, indicate that some other, more reactive species, probably a polymer, is formed at low temperatures. Infrared studies of matrix-isolated SiF_2–SiF_4 mixtures above and with other reactants (*13*) provide evidence for the existence of a fairly simple yet reactive species at about 35°K, possibly a dimeric, diradical form of SiF_2.

The polymer $(SiF_2)_n$ is a white-to-yellowish rubbery solid at room temperature. It is spontaneously inflammable in moist air, but reacts incompletely with water, liberating hydrogen and some silanes. It dissolves slowly in 10 percent HF and liberates hydrogen and silanes up to at least hexasilane (Si_6H_{14}). This is similar to the reaction of SiO with dilute HF (*14*). When heated from 200° to 350°C in a vacuum the polymer melts and slowly decomposes to a mixture of perfluorosilanes. When the mixture is monitored with a mass spectrometer, one can detect species up to at least $Si_{16}F_{34}$. From the pyrolysis products, it has been possible to isolate and characterize the compounds Si_3F_8 and Si_4F_{10}. The physical properties of these compounds are presented in Table 2; the high melting points and Trouton constants may indicate some association in the liquid and solid phases. This may be due to the polar nature of the Si–F bond.

Reactions of Silicon Difluoride

By analogy with carbenes, SiF_2 might act as either an electron donor or an electron acceptor, leading to a wide range of potential chemical reactions.

The low-temperature reaction between SiF_2 and BF_3, which is a strong Lewis acid, has been studied by Timms *et al.* (*15*). A series of compounds, BSi_nF_{2n+3}, with values of n ranging from 2 to 13, is formed, of which the two most abundant are Si_2BF_7 and Si_3BF_9. The structures of these two compounds have been established by examination of their ^{19}F and ^{11}B nuclear magnetic resonance spectra, as the perfluoroborosilanes $SiF_3SiF_2BF_2$ and $SiF_3SiF_2SiF_2BF_2$. No compound is found with one silicon atom, although SiF_3BF_2 has been recently prepared by Timms from the reaction of BF with SiF_4 (*16*). The perfluoroborosilanes are colorless liquids or solids; they ignite spontaneously in air and undergo hydrolysis readily.

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Table 1. The ν_2, bending, mode in SiF_2.

ν_2	Frequency (cm^{-1})
Ground state (ultraviolet) (*12*)	345
Ground state (microwave) (*11*)	343
1st excited state (ultraviolet) (*12*)	253

Table 2. Physical properties of perfluorosilanes and perfluoroborosilanes. The values for ρ (density), σ (surface tension), and N (refractive index) were taken from reference (*23*).

Compound	Reference	Melting point (°C)	Boiling point (°C)	Trouton's constant (entropy units)	ρ (g/ml)	σ ($dyne\text{-}cm^{-1}$)	$N^{20}{}_{C}$
Si_2F_6	(*22*)	− 18.6	− 18.9	25.6			
Si_3F_8	(*7*)	− 1.2	+ 42.0	27.8	1.665	12.53	1.3026
Si_4F_{10}	(*7*)	+ 66–68	+ 85.1	30.2	1.71		1.364
Si_2BF_7	(*15*)	0	+ 42		1.62	14.3	1.2975
Si_3BF_9	(*15*)	+ 11–12	+ 85		1.72		

Reaction with phosphorus trifluoride (PF_3) leads to a series of P-Si-F compounds, but these are unstable and decompose rapidly to perfluorosilanes and black P-F polymers.

Another characteristic reaction of carbenes is their addition to unsaturated systems to form cyclic, generally three-membered, systems. The reactions of SiF_2 with a number of unsaturated hydrocarbons have now been studied, and several important differences from normal carbenes have been found.

Benzene and SiF_2 form a yellow-brown polymer which, on distillation, at 140°C yields a series of compounds, $C_6H_6(SiF_2)_n$, where $n = 2$ to at least 8 (*17*). The most abundant of these, $C_6H_6Si_3F_6$, has been separated by gas chromatography and its structure has been identified by nuclear magnetic resonance (NMR) spectroscopy, chemical degradation, and elementary analysis. It is a bicyclic derivative of cyclohexadiene (Fig. 2). At room temperature the compound is a crystalline solid and is hydrolyzed by dilute hydrogen fluoride to 1,4-cyclohexadiene. Similar types of compounds are obtained from the reaction of SiF_2 with toluene.

Silicon difluoride also reacts with perfluorobenzene (*17*), but the products are not at all similar to those obtained from benzene. Blue flashes are visible during condensation of the reactants at −196°C and on warming them to −150°C. The main compound isolated is C_6SiF_8 which has been shown by infrared, ultraviolet, and NMR spectroscopy to be perfluorophenylsilane $C_6F_5SiF_3$. Other compounds isolated in small yields are $C_6F_4(SiF_3)_2$ and $C_6F_3(SiF_3)_3$. In all compounds the aromatic nucleus is retained.

Both types of behavior are detected in the reactions between SiF_2 and partially fluorinated benzenes; both monofluoro- and *p*-difluorobenzenes give small amounts of aromatic derivatives and also less volatile species believed to be SiF_2-bridged compounds.

The reaction of SiF_2 with ethylene yields two main products: $C_2H_4Si_2F_4$ and $C_4H_8Si_2F_4$ (*18*). These structures have been partially identified by NMR spectroscopy and appear to be disila-derivatives of cyclobutane and cyclohexane (Fig. 3).

Reactions between SiF_2 and various partially fluorinated ethylenes such as vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene have yielded several SiF_3-ethylene derivatives. Also some novel compounds have been obtained by the interaction of acetylene with SiF_2. One of these, $C_4H_4Si_2F_4$, may have an unsymmetrical structure $H_2C{=}CH\text{-}SiF_2\text{-}SiF_2\text{-}C{\equiv}CH$, while the next compound in the series, $C_4H_4Si_3F_6$, seems to be a bicyclic species (*19*) with the structure shown in Fig. 4.

Oxygen reacts with SiF_2 and gives a blue glow both in the gas phase and on cooling to −196°C. Hexafluorodisiloxane has been separated from the reaction products, and there remain several unidentified liquids believed to be both chain and cyclic fluorinated siloxanes. Sulphur dioxide reacts with SiF_2 to give sulphur and a similar complex mixture of polyfluorosiloxanes.

The monomers SiF_2, $SiCl_2$, $SiBr_2$, and SiI_2 have all been observed to form reactive polymers (*1–3*, *20*). Reactions of $SiCl_2$ have been investigated by Timms (*16*) and Schafer (*20*) and the $SiMe_2$ molecule has been studied by Skell and Goldstein and by Nefedov and Manakov (*21*). The long half-life

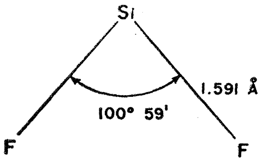

Fig. 1. Structure of SiF_2 as obtained from the microwave spectrum (*11*); $\mu = 1.23 \pm 0.015$ debye.

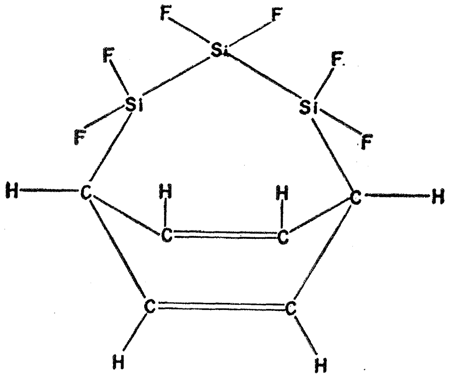

Fig. 2. Bicyclic derivatives of cyclohexadiene from benezene and SiF_2.

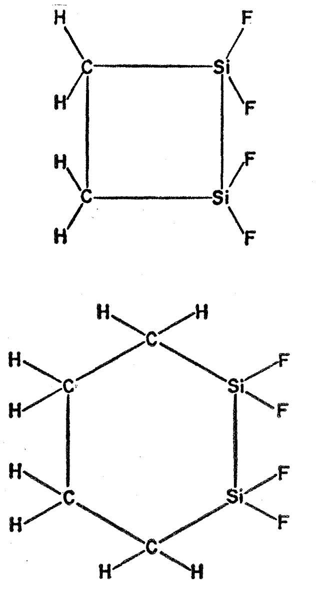

Fig. 3. Disila- derivatives of cyclobutane and cyclohexane.

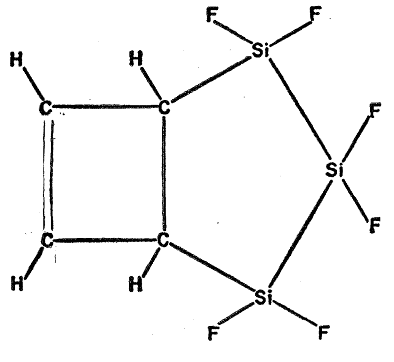

Fig. 4. Bicyclic species from the interacting of acetylene with SiF_2.

of SiF_2, however, appears unique among these divalent species. Thus, silicon difluoride opens up new possibilities for syntheses of previously known silicon-fluorine compounds and, in addition, leads to several novel types of organic and inorganic species not predicted from fluorocarbon chemistry or from the known chemistry of the other divalent silylenes.

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NEWS AND COMMENT

Medicine and Politics: A Fresh Look at the British Experience

London. Although few pieces of American social legislation have stirred more controversy before they became law, Medicare has been having a relatively quiet first year. In Britain, where health and hospital care has been nationalized for 20 years, controversy seems continuous. And a recently published book by a former Minister of Health, Enoch Powell, has added fuel to the fire.

A New Look at Medical Education[*] was written for a series of books planned primarily for the medical profession, and Powell takes an appropriately clinical tone. Powell, a Conservative, does not prescribe any sweeping changes of the National Health Service; rather, he sets out to explain it. In doing so he has a number of things to say about relations between politicians and professionals which extend to science and education as well as medicine and, in fact, have transatlantic application.

The analogy with the United States cannot be pushed too far. Under Medicare, the U.S. government acts essentially as paymaster and the organization of medicine has not been seriously affected. This differs, of course, from the situation in Britain, where, under the National Health Service, the government, on the one hand, operates the hospitals and employs hospital doctors and nurses and, on the other, controls the conditions of general practice through contracts with the overwhelming majority of G.P.'s.

Governmental responsibility is also divided differently in the two countries. In the United States legislative and executive powers are constitutionally separated, while in Britain the governing party's members in Parliament also hold the equivalent of American Cabinet and sub-Cabinet posts. These differences certainly cannot be discounted, but Powell makes several provocative general comments, which, if valid at all, are valid where representative government prevails, and Americans should find them worth considering.

Powell, for example, questions the assumption that a seat in the Cabinet gives a minister greater bargaining power in behalf of his department. Not so, says Powell: "The idea that members of a government extort by their weight and personal influence a larger or smaller share of national resources for their respective charges is grotesquely unreal. The complex balance of pressures—electoral, social, practical—that determine the rate at which a branch of public expenditure grows are little accessible to individual sway; and even if one individual could, by force of personality and advocacy, present the claims of his department to his colleagues with more emphasis and advocacy than another, that result would still not depend on whether he was 'called in' to Cabinet for the items in question or sat there as of right throughout."

Civil servants like to have their minister in the Cabinet because it elevates their own status and may, in fact, make some things easier for them. On the other hand, says Powell, the Cabinet member must devote much time to matters outside the concern of his own department, and this inevitably detracts from his performance of ministerial duties.

In the United States the histories of independent agencies such as the Atomic Energy Commission, the National Science Foundation, and especially the National Aeronautics and Space Administration show little to indicate that a place at the Cabinet table would have materially affected their fortunes. Advocates of giving the agencies which administer federal education and science programs Cabinet status, separately or in combination, might well consider Powell's pros and cons.

Powell also says that the belief that a government administrator should have a deep knowledge of the subject matter with which his department deals is a "popular fallacy," and is based on a misunderstanding of the function of the politician who heads a government department. "His job," says Powell, "as his description denotes, is

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[*] Pitman Medical Publishers, London.