

FLOW PYROLYSIS OF HEXAFLUORODISILANE AS A SOURCE OF HIGHLY REACTIVE DIFLUOROSILYLENE

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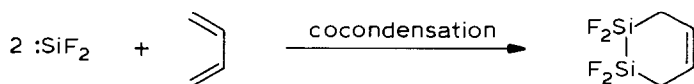
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Summary

Gas-phase fast-flow pyrolysis of Si_2F_6 at 670–720°C in a mixture with excess 1,3-butadiene led to the formation of high yields (56–75%) of 1,1-difluoro-1-silacyclopent-3-ene. A lower limit of $k_2 = 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the gas-phase addition of SiF_2 to butadiene at 700°C was estimated.

In this paper we report that hexafluorodisilane Si_2F_6 is a useful source of difluorosilylene for high temperature flow pyrolysis reaction studies and that under these conditions the reaction of SiF_2 with 1,3-butadiene is unexpectedly rapid.

In 1971 one of us wrote: "It is truly unfortunate that SiF_2 , the best characterized structural analog to carbenes, is also the least prone to undergo reaction in monomeric form; ..." [1]. This statement was prompted by the isolation of compounds containing two or more SiF_2 units as the preponderant products from the cocondensation at -196°C of $\text{SiF}_2/\text{SiF}_4$ mixtures with reaction substrates [2]. A pertinent example is the reaction with butadiene [3]:



A low reactivity for difluorosilylene was also suggested by its long life-time. The half-life of SiF_2 in the gas phase at room temperature for a mixture of 65% SiF_2 and 35% SiF_4 at 0.1 torr was found to be 150 s, unaffected by the presence of 2 torr of N_2 , BF_3 or CO [4]. A decrease in the lifetime of SiF_2 to 6 s in the presence of 1 torr

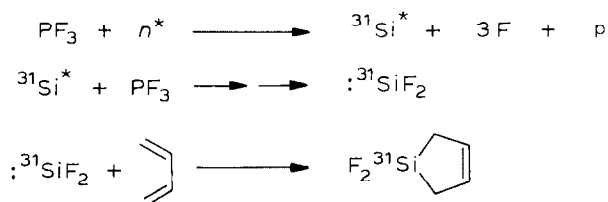
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of O_2 was attributed to rapid wall reactions, since no products were detected in the gas-phase. From these data upper limits can be deduced for the bimolecular rate constants of SiF_2 reactions with SiF_4 and O_2 , ca. $2 \times 10^3 M^{-1} s^{-1}$, with SiF_2 , ca. $1 \times 10^3 M^{-1} s^{-1}$, and with N_2 , BF_3 and CO , ca. $4 \times 10^2 M^{-1} s^{-1}$.

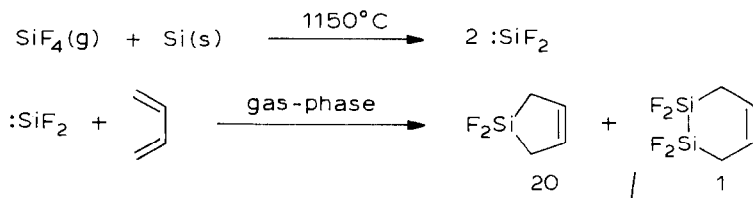
Recently the sluggish reactivity of SiF_2 has been confirmed by direct kinetic measurements at room temperature in a fast flow reactor, and upper limits of ca. $10^4 M^{-1} s^{-1}$ could be placed on the bimolecular rate constants for reactions with O_2 and H_2 [5]. The only rapid reactions of SiF_2 at ambient temperatures that have been observed were those with molecular fluorine and chlorine $k_2(F_2) 2.8 \pm 0.2 \times 10^8 M^{-1} s^{-1}$ and $k_2(Cl_2) 3.1 \pm 0.4 \times 10^8 M^{-1} s^{-1}$.

As early as 1972 direct reactions of SiF_2 with organic substrates were indicated by formation of a butadiene adduct containing a single SiF_2 unit, found by Tang and coworkers in a silicon atom gas-phase recoil experiment [6]. This was attributed to addition by nucleogenic difluorosilylene:



Despite this clear indication that SiF_2 could react in monomeric form, it was thought that the recoil-generated silylene might be in an excited electronic state, and even in 1978 it was written that: "It has not been established, however, that thermally generated SiF_2 undergoes reactions prior to dimerization." [7]. In the same year Seyferth put forth the contrasting view that many products containing two or more SiF_2 units from the reactions of difluorosilylene were due to secondary reactions, and that most reactions of difluorosilylene with olefins and acetylenes involved direct addition, followed by dimerization or reaction with further SiF_2 [8].

While the case for SiF_2 dimerization prior to reaction with added substrates has been reiterated [9,10], much evidence for reactions of monomeric SiF_2 in the gas-phase has accumulated recently [11–16]. Hwang and Liu found that when SiF_2 prepared by the Margrave comproportionation method was kept in contact with butadiene in the gas-phase for 25 min at room temperature, 1,1-difluoro-1-silacyclopent-3-ene was the predominant product, formed in $\geq 30\%$ yield together with only a small amount of the disilacyclohexene [12].

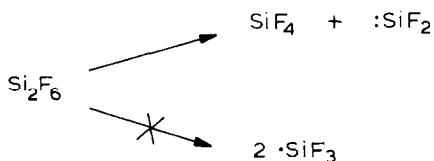


The contrast between the results obtained by Liu, and earlier Tang, for the reaction of SiF_2 with butadiene in the gas phase and those of Margrave for the same reaction under cocondensation conditions suggested that butadiene is an ideal

substrate for determining whether the reactions of SiF_2 can be studied under gas-phase fast-flow pyrolysis conditions. The formation of different products from gas-phase and condensed-phase processes established by earlier workers permitted an unambiguous assessment of the extent to which SiF_2 underwent reaction prior to condensation.

In the flow pyrolysis technique that has been so useful for the study of many silylene reactions [7,11,17], a gaseous mixture of silylene precursor and reaction substrate is passed rapidly through a hot zone under conditions sufficiently vigorous to generate the silylene but not so extreme that substrates or products are destroyed. The Margrave method for formation of SiF_2 employs temperatures (ca. 1100°C) that are too high for this purpose and gas-phase reaction studies have been carried out by mixing SiF_2 with substrates at room temperature with long contact times [18]. We therefore sought a different precursor for SiF_2 that could be converted at temperatures suitable for fast flow experiments, recognizing that addition reactions of difluorosilylene might prove to be too slow to be carried out in this manner.

As a source of SiF_2 we turned to a rather neglected reaction, pyrolysis of hexafluorodisilane Si_2F_6 . Some years ago it was found that the same polymer of SiF_2 is formed from pyrolysis of Si_2F_6 [19] as results from the high temperature reaction of SiF_4 and solid Si [20]. Ring and coworkers studied the flow pyrolysis of Si_2F_6 at 405°C (neat) and 415°C (1/80 mixture with Me_2SiH_2) [21]. From the production in quantitative yields of SiF_4 , it was concluded that α -elimination to SiF_2 occurred, rather than homolytic cleavage to silyl radicals.



The absence of Si-F or Si-H insertion products from the silylene led these workers to agree with the previous conclusions that SiF_2 is unreactive in the gas phase. It can be estimated that residence times in the hot zone of the order of 10^1 s were employed in these experiments.

We have subjected Si_2F_6 to fast flow pyrolysis in the presence of excess 1,3-butadiene at higher temperatures (670 – 720°C) and much shorter residence times (0.01 – 0.02 s) than were used by Ring. At 700°C , 3 torr total pressure, and 0.01 s contact time, the conversion of Si_2F_6 (26%) is sufficient for reaction studies in which products are formed in isolable quantities.

These are the same conditions, quite mild due to the short residence times, that have allowed the characterization of a wide variety of insertion and addition products from many silylenes [7,11,17]. The question has been, is SiF_2 sufficiently reactive to be trapped in the gas-phase on the short-time scale of such an experiment.

In our fast flow pyrolyses of Si_2F_6 in excess butadiene, 1,1-difluoro-1-silacyclopent-3-ene was formed in quite high yields (56–75%) and was the only fluorine-containing product found in addition to SiF_4 . This suggests that even with contact times as short as 0.01 s, reaction of SiF_2 with butadiene was complete prior to condensation. Had reaction occurred subsequent to condensation, 1,1,2,2-tetrafluoro-1,2-disilacyclohex-4-ene would have been found.

These data place an upper limit on the half-life of SiF_2 at 700°C in the presence of 3 torr butadiene of 0.02 s, and thus a lower limit on the bimolecular rate constant of $10^6 \text{ M}^{-1} \text{ s}^{-1}$. Recently rate constants in the 10^7 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$ range have been measured for SiCl_2 at room temperature [22].

The present experiments have thus established that flow pyrolysis of Si_2F_6 is a convenient source of SiF_2 that is highly reactive at the temperatures required for its efficient production from this precursor. This opens the door to studies of difluoro-silylene reactivity with many substrates under conditions sufficiently mild to allow primary products to survive. Thus a better understanding may be achieved of this interesting molecule whose chemistry has largely eluded workers in the field for two decades.

Experimental

Hexafluorodisilane was prepared by reaction of Si_2Cl_6 with ZnF_2 by the method of Schumb and Gamble [23].

The pyrolyses were carried out in a vacuum flow system whose hot zone was a 10 mm i.d. \times 18 cm quartz tube wrapped with ca. 22' of 26-gauge nichrome heating wire with an inner and outer layer of asbestos ribbon [24]. The temperature of the hot zone was measured with an iron-constantan thermocouple placed between the outer surface of the quartz tube and the inner layer of asbestos. The flow system was throttled downstream from the hot-zone by a copper disk with a 0.036" diameter orifice. Products were trapped ca. 12 cm from the hot-zone in a U-trap immersed in liquid nitrogen. A gaseous mixture of Si_2F_6 and 1,3-butadiene was delivered from a 1.3-liter reservoir through a ball-type flow meter. The pressure was measured just upstream from the hot-zone by a calibrated thermocouple gauge. Contact times t_c were calculated from the following equation:

$$t_c = V_H P_H t_H / nRT_H$$

in which: V_H = volume of hot zone; P_H = pressure in hot zone during reaction; t_H = total time for reaction mixture to pass through the hot zone; h = total number of mol of reaction mixture; R = gas constant; and T_H = temperature of hot zone.

In each pyrolysis experiment a mixture of 0.65 g Si_2F_6 (3.8 mmol) and 2.07 or 4.13 g 1,3- C_4H_6 (38 or 76 mmol) was employed. The reaction mixture was passed through the hot zone at 3 torr total pressure over a period of 7.5 min.

Product mixtures were separated by trap-to-trap distillation in another portion of the same vacuum line to which the flow pyrolysis system was attached. SiF_4 , unreacted Si_2F_6 , and 1,3- C_4H_6 passed a -77°C (dry ice/acetone) trap and were stopped at -196°C (liq. N_2). This mixture was passed through a -97°C trap (MeOH slush) which stopped the Si_2F_6 that was subsequently transferred to a 1.3 l bulb and its pressure determined.

The contents of the -77°C trap were subjected to vapor chromatographic analysis on a 12' \times 2 mm (i.d.) glass column with 5% OV-17 silicone oil on GAW DMCS Chromosorb 100/110 diatomaceous earth, 55°C , $25 \text{ cm}^3 \text{ min}^{-1}$ He flow. The only fluorine-containing product (butadiene dimers were also detected) was 1,1-difluoro-1-silacyclopent-3-ene (see Table 1 for yields): ^1H NMR (300 MHz, Varian XL-300) (C_6D_6) δ 1.059 (dt, 4H, J_{32} 1.1, $J_{\text{F},2}$ 3.6, CH_2) 5.650 (tt, 2H, $J_{2,3}$ 1.5, $J_{\text{F},3}$ 4.6, $-\text{CH}=\text{CH}-$); $^{25} \text{ } ^{19}\text{F}$ NMR (282 MHz, Varian XL-300) (C_6D_6 , external

TABLE 1

YIELD OF 1,1-DIFLUORO-1-SILACYCLOPENT-3-ENE FROM FLOW PYROLYSIS OF HEXAFLUORODISILANE IN MIXTURES WITH 1,3-BUTADIENE

$T(^{\circ}\text{C})$	Ratio $\text{C}_4\text{H}_6/\text{Si}_2\text{F}_6^a$	Contact time (s)	Conversion of Si_2F_6 (%)	Yield of $\text{F}_2\text{SiCH}_2\text{CHCH}_2$ (% absolute) ^b
670	20	0.02	5	75
700	10	0.01	26	61
720	10	0.02	38	56

^a All experiments employed 3.8 mmol Si_2F_6 and 3 torr total pressure. ^b Yields based on unrecovered Si_2F_6 .

standard, C_6F_6 0 ppm) δ 24.09 (multiplet of ≥ 5 lines, collapsed to sharp singlet upon proton decoupling); MS (70 eV Finnegan 3200 GC/MS) m/e 126 (M^+ , 27), 101(3.4) 91(46), 66(5.4), 65(20), 54(base, 100).

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