THE REACTION OF PROPENE WITH DIFLUOROSILYLENE

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Summary

The reactions between difluorosilylene and propene in both the gas phase and under cocondensation conditions have been studied. In the gas phase, SiF_2 gave products containing only one SiF_2 unit, and thus it behaved like a carbene. However, in the cocondensation experiment a number of volatile products containing SiF_2SiF_2 units were obtained in addition to the polymers. A comparison of the results from these different experimental conditions provides some insight of the reaction mechanism.

The "addition" reactions which difluorosilylene undergoes with unsaturated organic compounds have for many years been interpreted in terms of a mechanism involving the initial formation of $\cdot(SiF_2)_n\cdot$ diradicals (in most cases $n = 2$) at −196°C [1—3]. Other mechanistic alternatives involving difluorosilirane and difluorosilirene intermediates have been proposed [4], but these had not gained much support until Seyferth and Duncan recently reported the synthesis and some chemistry of 1,1-difluoro-2,2,3,3-tetramethylsilirane [5]. The relevance of Seyferth's work to the mechanism of difluorosilylene reactions effected by the cocondensation method was further supported by a ^{29}Si NMR study of the copolymer formed in the propene/SiF_2 cocondensation reaction [6]. However, there still were some uncertain points which needed to be clarified [7].

First of all, while approximately 70% of the total products of the reaction between propene and SiF_2 were found to be polymers involving alternating C_3H_6 and SiF_2 units, all cocondensation reactions of alkenes and alkynes studied so far gave only one type of volatile product, products involving the SiF_2SiF_2 unit [1—3]. Secondly, we recently found that in the gas phase reaction of 1,3-butadiene [8], monomeric, gaseous SiF_2 was the reactive species and the product, 1,1-difluorosilacyclopent-3-ene, differed from the products of the same reaction as effected by cocondensation (all contained SiF_2SiF_2 units). These observations seemed to suggest that the reaction of SiF_2 in the gas phase and in cocondensation experiments may proceed by different pathways.

One of the difficulties involved in the study of the reactions of difluorosilylene with alkenes is the complexity of the isomers of the six-membered ring products disilacyclohexanes. We recently reported the results of our study of the reaction of vinyl chloride and difluorosilylene, in which the analysis of the isomers of the 1,2-disilacyclohexane product by examining their fluxional behavior in the ^{19}F NMR spectra was successful [7]. Such an analysis should also obtain in the case of the reaction with propene.

It is for these reasons that we decided to study the reaction with propene both in the gas phase and under cocondensation conditions. During the time this paper was in preparation Thompson et al. reported their study of the cocondensation of SiF_2 with methyl-substituted ethylenes [14].

Experimental

Cocondensation experiments

Propene was prepared by the standard method [9] and its purity was checked by IR spectroscopy before use. Silicon tetrafluoride was a commercial product used without further purification. The apparatus and experimental details have been described elsewhere [10]. Separation of the volatile products from this reaction by trap-to-trap fractionation was carried out as follows: (i) excess SiF_4 and C_3H_6 were removed by pumping through a cold trap kept at $-112°C$, (ii) fractions volatile at $-22°C$ and collected at various temperatures from $-45°C$ to $-f$)f all contained products III, IV and V, and (iii) the fraction volatile at at room temperature collected at $-22°C$ contained I and II. Pure I was obtained by GC separation. A preparative column of diisodecyl phthalate was used for the separation. The total yield of products based on the propene consumption was found to be about 35%; 30% of this material was composed of volatile products.

Gas phase reactions

The gas phase reactions were carried out in a 6 l bulb made of Pyrex glass. The bulb was connected to the gas inlets and the pressure-measuring device of a greaseless vacuum system [13]. Propene and SiF_2 of desired quantities were introduced into the bulb separately by needle value controls. The quantity of SiF_2 could be estimated as the yield of SiF_2 from SiF_4 was determined to be $\sim$50 percent under the experimental conditions [1]. The gas mixture (total pressure $\simeq$2 Torr) was allowed to react in the closed system for 25 minutes (roughly ten times the half-life of SiF_2), before it was pumped out for fractionation. The procedures were repeated until about 10 mmol of each reagent was used in the reaction.
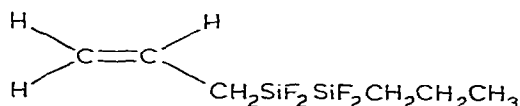
Spectra

All NMR spectra were obtained using a JEOL FX-100 spectrometer operating at 99.6, 93.7 and 25.1 MHz for ^1H, ^{19}F and ^{13}C spectra, respectively. In all cases $CDCl_3$ was used as the solvent. ^1H and ^{13}C chemical shifts were measured with TMS as the internal reference, ^{19}F chemical shifts were measured in ppm upfield from the internal reference CCl_3F. Mass spectra (12 eV) were recorded on a JMS-100 mass spectrometer.

Results and discussion

Cocondensation reaction

The major portion of the volatile products (accounting for over 80% of the total volatile products) from the cocondensation experiment was collected at −22°C during the fractionation. This fraction contains three compounds. They were identified unequivocally by means of mass spectrometry and ^{1}H and ^{19}F NMR spectroscopy to be I and II (*trans* and *cis*).
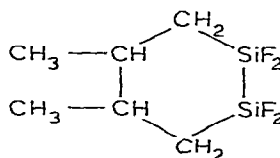
$$\text{(I)} \qquad\qquad (\text{II}, trans, cis)$$

Careful fractionation resulted in another fraction which was volatile at −64°C and was collected at −90°C. This small fraction accounted for less than 10% of the total yield of volatile products. The mass spectrum and NMR spectral data conclusively indicated that the compound has the 1,2-disilacyclobutane structure III. The spectral properties of I, II and III are essentially the same as those reported by Thompson [14] and for this reason they will not be repeated here.
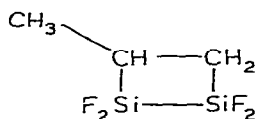
In addition to these three compounds there are minor products with volatilities similar to that of III present as "impurities" in all fractions collected between −45° to −90°C. We found that after separation from the major products I and II (by passing through a trap at −22°C) a fraction containing mainly such "impurities" could be obtained at −78°C by prolonged pumping through a trap kept at −45°C. The relative abundance of this fraction was about 10% of the total yield of volatile products. The mass spectrum of this fraction showed the highest m/e at 126 and 127. The ^{1}H NMR spectrum resembled that of compound I, but the ^{19}F NMR spectrum was completely different. Two resonances appeared at 137.98 and 139.45 ppm, respectively, the former a triplet of multiplets with triplet coupling of 3.0 Hz, the latter a broadened triplet with a coupling constant of 2.8 Hz. When proton-decoupling was applied, both resonances reduced to singlets. When the fraction was further fractionated by pumping through a trap at −64°C and collected at −196°C, two fractions could be obtained. The ^{19}F NMR spectra of these fractions showed both resonances to be present but in different intensity ratio. All these observations seems to indicate that two different compounds containing SiF$_2$ units are present in these fractions. The structures of these two compounds were determined by means of selective proton-decoupling to be IV and V.

$$H_B \diagdown \atop H_C \diagup C = C \diagup \atop \diagdown {}^{H_A} \atop CH_2SiF_3 \qquad , CH_3CH_2CH_2SiF_3$$

4   7   6   5

(IV)   (V)

As can be seen from Fig. 1, the complex peaks for H(4) at δ 2.15 ppm become a quartet when the sample is irradiated at the position of the ABC signals (for the vinyl protons in IV), with all other signals remaining unchanged. Also, when irradiation was applied at the position of H(4) (δ 2.15 ppm), only the ABC pattern is simplified. On the other hand, when the broadened sextet was irradiated (H(6), δ 1.78 ppm), the triplet at δ 1.28 ppm (assigned to H(7)) became a singlet, and the partially hidden complex spectrum (assigned to H(5)) at δ 1.10 ppm was simplified to a quartet. The rest of the spectrum remained unchanged.

All these observations strongly support our structural assignment for IV and V. One further piece of evidence comes from the measurement of H—F coupling constants. The coupling constants of H(4)/SiF$_3$ and H(5)/SiF$_3$ obtained from these selectively decoupled ^{1}H spectra are in agreement with those obtained from the ^{19}F NMR spectra: 2.8 and 3.0 Hz, respectively.

The proton-decoupled ^{13}C NMR spectra also support this assignment. Two quartets at δ 15.49 and 20.11 ppm are assigned to C(5) and C(4), respectively (coupled by adjacent SiF$_3$ groups), two singlets at δ 21.52 and 23.23 ppm are

Fig. 1. ^{1}H NMR spectra of a mixture of IV and V, (a) undecoupled, (b) irradiated at δ 5.5 ppm, (c) irradiated at δ 2.15 ppm, and (d) irradiated at δ 1.78 ppm.

assigned to C(7) and C(6), respectively, and the two singlets at δ 118.97 and 126.60 ppm, are undoubtedly the signals of the unsaturated carbon atoms in compound IV.

Also, we note that the intensity ratio of the two compounds in the ^{1}H NMR spectra agree with those in the ^{19}F NMR spectra of all samples with various relative abundances. All the NMR data are collected in Table 1.

The non-volatile product, the polymers, accounts for 60—70% of the total reaction yield. Only a portion of the polymers is soluble in chloroform. The IR spectrum of this portion of the polymer showed ν(C—H) (2800—3000s cm^{-1}), ν(C—C) (1100—1300m cm^{-1}) and ν(Si—F) (800—1000s cm^{-1}). The ^{1}H NMR spectrum showed only a broadened resonance around δ 1.50 ppm and no signals due to unsaturated C—H protons were present. Thompson et al. recently studied this polymer by ^{29}Si NMR spectroscopy and reported that the polymer consisted of $(C_3H_6SiF_2)_n$ units [6]. We find that the proton-noise decoupled ^{19}F NMR spectrum of the soluble portion of the polymer shows two sets of the AB system centering at 142.76, 146.36 ppm and 143.98, 144.93 ppm, respectively, both AB patterns showing J(AB) = 19.5 Hz. The AB spectra are caused by the chiral character of the methyne carbon —*CH(CH$_3$)SiF$_2$—; whereas the two sets of AB spectra van be interpreted as the two distinct chemical environments caused by the diasteric combinations when the neighboring chiral centers in both sides of each SiF$_2$ unit are considered. Therefore, the spectrum is inconsistent with the head-to-tail structure and suggest that the polymer is most likely an atactic one [6].

The mass spectrum of this polymer (sample heated to about 100°C under vacuum) showed mass peaks up to about m/e 1000. The spectrum consisted of two types of repeating patterns of mass peaks differing by 108 $(C_3H_6SiF_2)$ up from m/e 175 and 193, respectively. All peaks within the range of these repeating patterns can be interrelated by a mass difference of either 66 (SiF$_2$) or 42 (C$_3$H$_6$). The mass peaks at 175 (—SiF$_2$CH(CH$_3$)CH$_2$SiF$_2$H) and 193 (—SiF$_2$CH(CH$_3$)CH$_2$SiF$_3$) may indicate that the termination of the polymerization occurs when the radical chain abstracts either an F or H atom.

TABLE 1

NMR DATA OF COMPOUNDS IV, V, VI, VII AND VIII

| Compound	^{1}H (δ ppm)		^{19}F (ppm)	^{13}C (δ ppm) [a]	
IV	vinyl H	5 ~ 6 (ABC)	SiF$_3$ 139.45 (t, br)	C=C	118.97 (s)
					126.60 (s)
	allyl H	2.15 (d, q)		CH$_2$SiF$_3$	20.11 (q)
V	CH$_2$SiF$_3$	1.10 (m)	SiF$_3$ 137.98 (t, m)	CH$_2$SiF$_3$	15.49 (q)
	CH$_2$CH$_2$SiF$_3$	1.78 (sext)		CH$_2$CH$_2$SiF$_3$	23.23 (s)
	CH$_3$	1.28 (t)		CH$_3$	21.52 (s)
VI	CH$_3$	1.94 (s, br)	SiF$_3$ 141.10 (d, q)		
	vinyl H	6.80 / 5.44 (AB)			
VII	CH$_3$	1.94 (s, br)	SiF$_3$ 136.80 (t, q)		
	vinyl H	5.90, 5.60 (m, br)			
VIII	CH$_3$	1.05 (d)	SiF$_3$ 142.20 (d)		
	CH	0.90 (m)			

[a] Proton-noise decoupled.

Gas phase reaction

The gas phase reaction of propene was carried out using the same procedures as were used in the reaction with butadiene [8]. About 10 mmol of C_3H_6 was used in the reaction and the total yield, based on the amount of C_3H_6 consummed, was $\leqslant 20\%$. There was a thin layer of polymer formed on the wall of the reaction bulb. The volatile products accounted for only 5% of the total yield. They were volatile at $-45°C$ and collected at $-90°C$.

The reaction appears very complicated. At least four volatile products have been identified by the mass and ^1H and ^{19}F NMR spectra. One is compound IV, which was also obtained in the cocondensation experiment. All of these compounds were not isolated as pure materials. Careful fractionation merely resulted in fractions with different proportions of the components. The ^{19}F NMR spectra showed four areas of resonance which varied in relative intensities in different samples and did not change when mutual F—F decoupling was applied. These features show clearly that the four resonances represent four independent compounds. Considering a mixture of four compounds, the mass spectrum appears remarkably simple. The highest mass peak at m/e 126 corresponds to a molecular formula $C_3H_5SiF_3$. However, the peaks at 127 and 128 are clearly more intense than the normal isotopic $p + 1$ and $p + 2$ peaks for a parent ion of $C_3H_5SiF_3$. This would suggest the existence of another molecular formula, $C_3H_7SiF_3$.

The ^1H NMR spectrum of the mixture was rather complex. However, a number of typical features made the assignment possible. It showed, in addition to the known spectrum of compound IV, a broad singlet at δ 1.94 ppm and an AB system for *trans* olefinic protons $(J(AB) = 19\ Hz)$ at δ 6.80 and 5.44 ppm. The A part of the system consisted of two quartets $(J = 6.5\ Hz)$, while the B part consisted of two complex multiplets. The spectrum is quite typical for structures with the $CH_3CH=CH-$ moiety [3]. We therefore assign this part of the spectrum to compound VI. In agreement with this, the ^{19}F NMR spectrum


(VI)
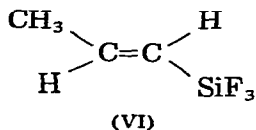
showed a doublet $(J = 3.3\ Hz)$ of quartets $(J = 1.3\ Hz)$ at 141.1 ppm which reduced to a singlet when ^1H-decoupling was applied. It is known that $J(H—F)$ of *cis* $CH=CSiF_3$ is very small $(\leqslant 1\ Hz)$ [11,12].

In the ^{19}F spectrum there was a triplet $(J = 4.9\ Hz)$ of quartets $(J = 1.0\ Hz)$ at 136.8 ppm, which suggests the existence of the *cis* isomer VII since it is known that the H—F coupling constants of *trans* $CH=CSiF_3$ and $=C\overset{\diagup SiF_3}{\diagdown H}$

are of the same magnitude [11,12].

(VII)
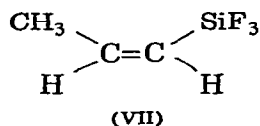
In agreement with this, the ^{1}H NMR spectrum showed two broadened complex peaks at δ 5.90 and 5.60 ppm, respectively, for the olefinic protons, and the signal for the CH$_3$ protons was obviously merged into the broad singlet at δ 1.94 ppm. There remained a doublet (J = 7 Hz) at δ 1.05 ppm and a broad complex signal at about δ 0.90 ppm. In the ^{19}F NMR spectrum there also remained a doublet (J = 3.8 Hz) at 142.2 ppm which reduced to a singlet on ^{1}H-decoupling. Considering a molecular formula of C$_3$H$_7$SiF$_3$ as suggested by the mass spectrum, we tentatively assign these spectra to compound VIII [15].

CH$_3$\
     \>CH—SiF$_3$
CH$_3$/
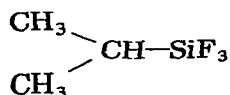
(VIII)

Reaction mechanism

Since all products obtained from the gas phase reaction with propene are compounds which contain only one SiF$_2$ unit, the reaction in the gas phase can best be explained in terms of a silirane mechanism:
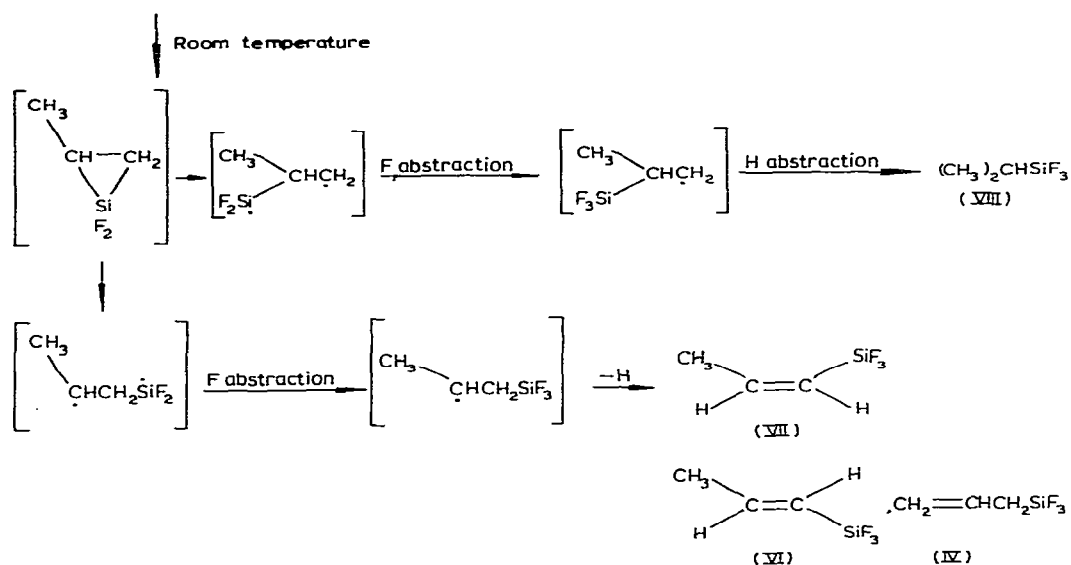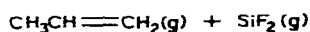

Since all identified products contain a SiF$_3$ unit, one may argue that the products could have been formed from an initial attack of SiF$_3$ radicals instead of SiF$_2$. It is known that SiF$_2$ does not easily abstract F from SiF$_4$ in the gas phase [1]. On the other hand the radical species ˙SiF$_2$R is expected to abstract a fluorine atom readily as can be verified by the intramolecular F-abstraction observed in a number of reactions [1]. Furthermore, under the same gas phase reaction conditions, no products resulted from SiF$_3$ attack were observed in the reactions with butadiene, vinyl fluoride, vinyl chloride and difluoroethylenes [13], where facile pathways for intramolecular rearrangement were avail-

able. We therefore propose the above mechanism, although the source of the abstracted F atoms cannot be determined unambiguously. However, if one considers that the abstracted F atoms came from SiF_4, the generation of $\cdot SiF_3$ would make the involvement of direct attack by $\cdot SiF_3$ radicals a possibility that cannot be ruled out.

If F-atom abstraction does exist, the fact that it results in the SiF_3 groups rather than fluorocarbons is understandable in view of the formation of exceedingly strong Si—F bonds in the former case. Also, the abstraction of F by the SiF_2 groups of

$$CH_3\diagdown \dot{C}HCH_2\dot{S}iF_2 \text{ and } \begin{array}{c} CH_3\diagdown \\ F_2\dot{S}i \diagup \end{array}CH\dot{C}H_2$$
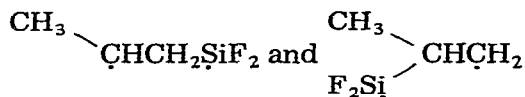
is thermodynamically more favored than the abstraction of an H atom, and the reverse is true for

$$CH_3\diagdown \dot{C}HCH_2SiF_3 \text{ and } \begin{array}{c} CH_3\diagdown \\ F_3Si \diagup \end{array}CH\dot{C}H_2$$
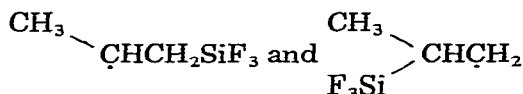
(Si—F 135 kcal/mol, C—F 119 kcal/mol, Si—H 55 kcal/mol, C—H 98 kcal/mol). However, it is rather surprising that only IV and no V was obtained in the gas
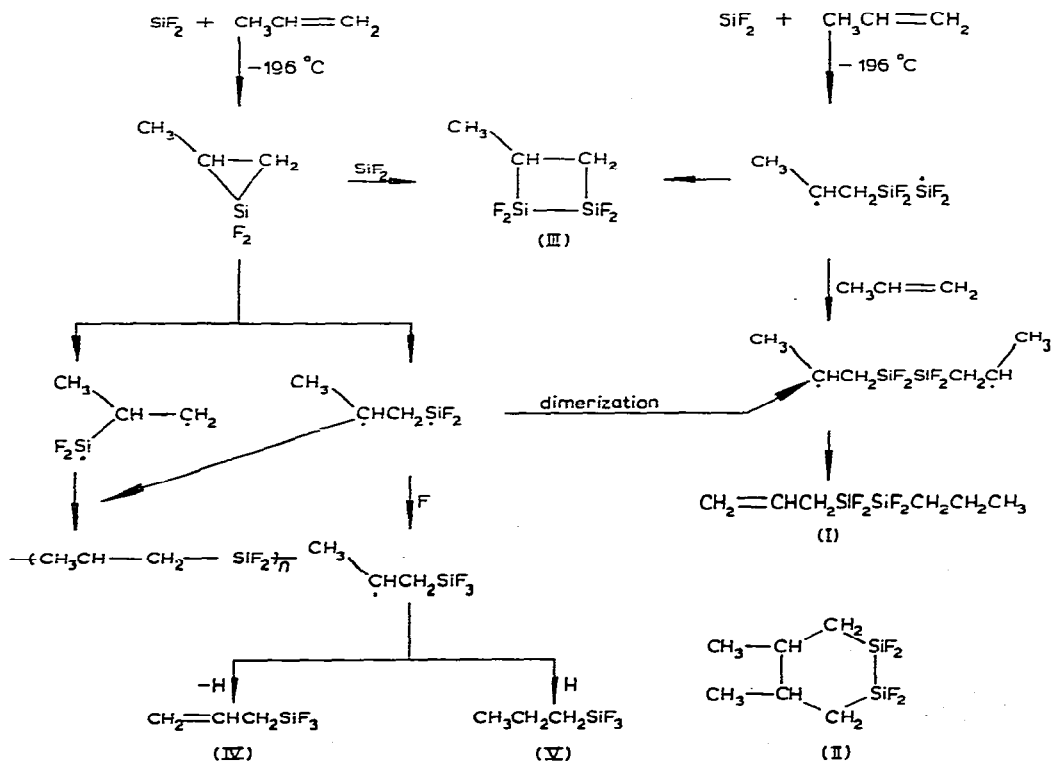
phase reaction. Although there has been no further evidence, this may reflect
the tendency of $\underset{\displaystyle CH_3}{\diagdown} CHCH_2SiF_3$ to eliminate one H more readily than

$$F_3Si \diagdown \underset{CH_3}{\diagup} CHCH_2$$
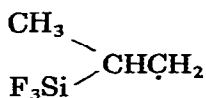
In the case of the cocondensation process, the situation is much more complicated. Unlike the products found in the gas phase reaction, all main volatile products in the cocondensation reaction contain a $-SiF_2SiF_2-$ unit. Together with the known fact that SiF_2 forms $\cdot(SiF_2)_n\cdot$ diradicals under the cocondensation conditions [1], it seems inadequate not to include the $\cdot SiF_2SiF_2\cdot$ diradical mechanism as an important pathway in the formation of the volatile products observed [13]. On the other hand, since the polymers, which account for over 65% of the total reaction products in the cocondensation experiment, appear to have mainly the $-(CH_3CHCH_2SiF_2)_n$-structure, it seems reasonable to assume that, at least for the present case, the silirane mechanism as postulated by Seyferth [5] and Thompson [6] would also play an important role in the formation of the volatile products in cocondensation reactions.

Acknowledgement

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