Laser-Induced Explosive Decomposition of (Fluoromethyl)silanes: Reductive Chemistry Initiated by Laser Photolysis

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The explosive decomposition of the (fluoromethyl)silanes H_2CFSiH_3, HCF_2SiH_3, CF_3,SiH_3, and $(CF_3)_2SiH_2$, which furnishes Si/C/F/H-containing deposits, has been induced by irradiation with a single CO_2 laser pulse at pressures of 0.1–6.7 kPa. The gaseous decomposition products are hydrocarbons (CH_4 and C_2H_2) and silanes rich in fluorine (SiF_4 and $HSiF_3$), which indicate an efficient gas-phase reduction of the strong C–F bond. The composition of the gas-phase products, investigated by IR and NMR spectroscopy, and that of concomitantly formed deposits, investigated by Raman and IR spectroscopy, depends significantly on both the parent molecule and its pressure. Amorphous and graphitic carbon, silicon carbide, organosilicon polymers, and hydrogenated amorphous silicon were detected. The analysis of the gaseous products led to a mechanism which suggests that the laser-induced decomposition and the conventional thermolysis of fluoromethylsilanes share common initial steps.

Introduction

New preparative entries[1-4] make (trifluoromethyl)silicon compounds now easily available: they are stable gases at atmospheric pressure and ambient temperature, but their laser photochemistry was only briefly studied for (trifluoromethyl)silane.[5] Laser-induced decomposition pathways for these compounds can be inferred from their known thermal behavior[6,7] and some pertinent data on similar compounds.

((Polyfluoro)methyl)silanes, $H_{3-n}CF_nSiH_3$, constituted of fluorocarbon and silane moieties may have a tendency to decompose in significant heterogeneous steps, which happen with fluorocarbons,[8] silane,[9] or methylsilane (H_3CSiH_3).[10] These heterogeneous processes occurring during the thermal decomposition of alkylsilanes $RSiH_3$ (R = alkyl) involve radicals and can be efficiently avoided using a shock-tube technique or laser radiation. Nonradical alternatives are 1,1-H_2, 1,2-H_2, and alkane eliminations.[11-13]

With ((polyfluoro)methyl)silanes different channels may operate as well. These compounds are susceptible to structural reorganization upon heating, due to an affinity with silicon for halogen,[14-16] and they can undergo thermal extrusion of carbenes, which subsequently insert into the Si–H bonds.[5,6] A preference for any of the envisaged mechanisms not only will account for different volatile products but can also be expected to have an impact on the composition (and perhaps modification) of the deposit. Such deposits were found to be formed in all thermal- or laser-induced decomposition processes of organosilanes. (Fluoromethyl)- or ((polyfluoro)methyl)silanes might suit demands for deposition of Si/C/F/H films recently prepared by laser-[17] or glow-discharge-induced[18] decomposition of mixtures of silane with fluorocarbons. They are revealed[18] to have promising photovoltaic properties.

We report on the explosive laser-induced decomposition of four fluoro-containing silanes H_2CFSiH_3 (I), HCF_2SiH_3 (II), CF_3SiH_3 (III), and $(CF_3)_2SiH_2$ (IV) and of methylsilane (V), all of which possess absorption bands in the emission region of a CO_2 laser. This decomposition occurs in the gas phase without heterogeneous reaction steps. The correlation between the compositions of gaseous and solid products of the laser decomposition, the discussion of the decomposition modes, and the examination of the prop-

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Table I. IR Spectral Parameters of (Fluoromethyl)silanes

compd	vibrational mode	absorptivity, $kPa \cdot cm^{-1}$ (at abs max, cm^{-1})	irradiation laser line (frequency, cm^{-1})	absorptivity at irradiating wavenumber, $kPa \cdot cm^{-1}$
CF_3SiH_3	$\nu_{as}(CF_3)$	0.38 (1110)	R(26)[a] (1082.3)	0.016
	$\delta_s(SiH_3)$	0.23 (899)	P(48)[b] (916.6)	0.028
HCF_2SiH_3	$\delta_s(SiH_3)$	0.24 (916)	P(42)[b] (922.9)	0.110
	$\nu_{as}(CF_2)$	0.17 (1041)	P(42)[a] (1025.3)	0.090
H_2CFSiH_3	$\delta_s(SiH_3)$	0.19 (927)	P(38)[b] (927.0)	0.190
$(CF_3)_2SiH_2$	$\delta(SiH_2)$	0.062 (917)	P(42)[b] (922.9)	0.050

[a] $00^01 \rightarrow 02^00$ transition. [b] $00^01 \rightarrow 10^00$ transition.

erties of the deposited materials are a broad extension of our note[5] on the laser decomposition of (trifluoromethyl)-silane.

Experimental Section

The experiments were performed using a tunable pulsed CO_2 laser operated on appropriate lines of the $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$ transition with a repetition rate of 1 Hz. The irradiating wavelengths, checked with a Model 16-A spectrum analyzer (Optical Engineering Co.), were chosen to achieve efficient absorption in (fluoromethyl)silanes (Table I). The CO_2–N_2–He (4:8:12) atmospheric gas mixture gave a pulse consisting of a sharp spike (~150 ns) followed by a tail that extended for about 1 μs. The energy of the incident beam was alternated by introducing polyethylene sheets of various thicknesses. Pulse energies were measured either with an RJ-7620 energy ratiometer (Laser Precision Corp.) or with a laser energy pyroceramic sensor (Charles University, Model ml-1JH).

The absorption of the radiation from particular laser lines of the $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$ transitions was measured at pressures of 0.1–0.3 kPa and pulse energies <0.05 J to avoid decomposition.

The reactor was a stainless steel tube (11 cm long, i.d. of 3.5 cm) equipped with NaCl windows which were attached with a Lukopren seal and had a valve for connection to a standard vacuum line which was located at the center of its body. The gaseous silanes (in the presence or absence of a gaseous scavenger of intermediate species) were introduced into the evacuated reactor and irradiated either with 1 or up to more than 10^3 unfocused pulses with fluences in the range 0.1–0.9 $J \cdot cm^{-2}$.

The IR spectra before and after irradiation were recorded with a Specord IR-75 infrared spectrometer. Gaseous reaction mixtures were also analyzed using a Shimadzu Model QP 1000 quadrupole mass spectrometer (columns packed with Porapak P or Porapak S, helium carrier, temperature programmed from 15 to 150 °C).

Amounts of gaseous reaction products were determined via the absorptivity of diagnostic (strong, nonoverlapping) bands by comparison with their molar absorptivities (cm^{-1}, 10^3 kPa^{-1} cm^{-1}): CH_4 (1300 or 3000, 13), HC≡CH (730, 94; 3260, 4.5), SiF_4 (1030, 834; 1020, 504), $SiHF_3$ (840, 79.7; 990, 451), C_2F_4 (1180 or 1340, 200) and C_2HF_3 (1790, 40). The absorptivities of these authentic samples were measured by employing cells of 10- and 0.8-cm path lengths.

Gaseous products condensable at −196 °C were furthermore qualitatively analyzed with a Nicolet 7199 FTIR spectrometer employing a small absorption cell of 8-cm length and 2-cm inner diameter. They were also studied by ^1H and ^{19}F NMR spectroscopy using C_6D_6 as solvent and employing a Bruker AC 250 spectrometer.

IR spectra of the deposit on NaCl windows were measured after evacuation of the reactor. Raman spectra of the solids were measured at room temperature using the 514.5-nm line of an Ar^+ laser for excitation. Near-backscattering was employed, and the laser beam was focused by a cylindrical lens to minimize sample heating. The scattered light was analyzed with a double grating spectrometer equipped with standard photon-counting detection.

Reference samples used for the analyses of the reaction mixtures were either purchased (methane, ethylene, Technoplyn), taken from the laboratory stock (tetrafluoroethene, trifluoroethene), or prepared. Trifluorosilane and tetrafluorosilane were obtained by a treatment of appropriate chlorosilanes with SbF_3/$SbCl_5$ reagents as reported for $HSiF_3$ in ref 19.

Methylsilane (V) was obtained by reduction of methyltrichlorosilane with sodium bis(2-methoxyethoxy)hydridoaluminate in a toluene solution using a standard vacuum line procedure. Its purity was checked by GC/MS and IR spectroscopy. The following (fluoromethyl)silanes were prepared according to reported procedures: H_2CFSiH_3 (I),[20] HCF_2SiH_3 (II),[7] CF_3SiH_3 (III),[2] and $(CF_3)_2SiH_2$ (IV).[6]

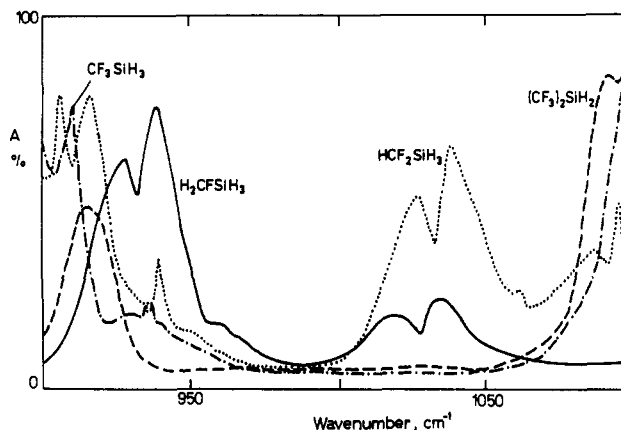

Figure 1. Gas-phase (0.3–0.4 kPa) IR spectra of (fluoromethyl)silanes in the region of emission of a CO_2 laser.

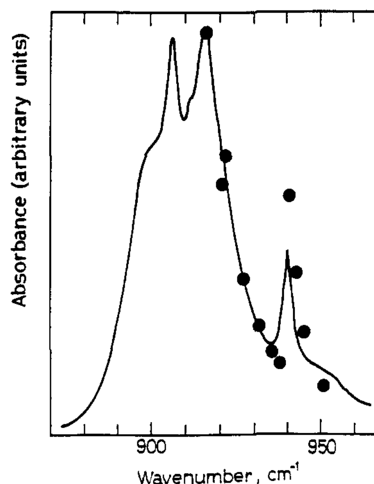

Figure 2. IR spectrum of HCF_2SiH_3 (solid line) compared to laser absorption data normalized to that at 916.6 cm^{-1}.

Results

The (fluoromethyl)silanes CF_3SiH_3, HCF_2SiH_3, H_2CFSiH_3, and $(CF_3)_2SiH_2$ exert absorption bands below 950 and above 1000 cm^{-1} (Figure 1) in the region of CO_2 laser emission, which belong to the vibrational modes of the SiH_n and H_nCF_{3-n} moieties. The absorption of laser radiation in all compounds nearly parallels the IR absorption curves, as is illustrated for II (Figure 2).

Infrared multiphoton decomposition of the (fluoromethyl)silanes I–IV can be induced at pressures of 0.1–6.7 kPa with appropriate irradiating lines tuned to absorption bands (Table I) at fluences ~0.2–0.9 $J \cdot cm^{-2}$. The irradiation with a single pulse results in an explosive reaction when the pressure exceeds a certain limit, which depends on the laser fluence and the wavelength. The explosion limit pressure of I–IV increases as the laser fluence decreases (Figure 3), and below this threshold some noticeable chemical changes can be detected only after

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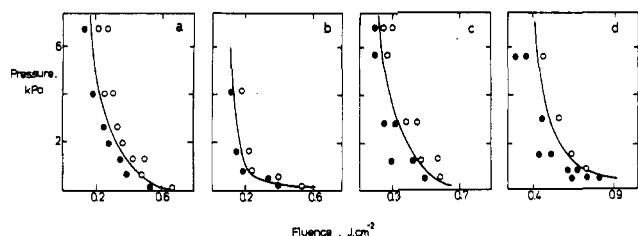

Figure 3. Pressure vs laser fluence diagram of the explosion limit for IRMPD of CF_3SiH_3 (a), HCF_2SiH_3 (b), H_2CFSiH_3 (c), and $(CF_3)_2SiH_2$ (d). Irradiating wavelengths in the given order are 916.6, 1025.3, 927.0, and 922.9 cm^{-1}. Empty and full circles relate to explosive reaction and no reaction, respectively.

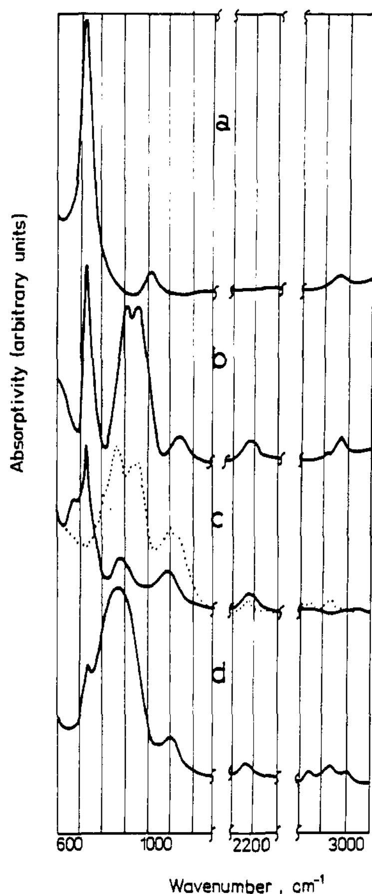

Figure 4. IR spectra of the deposit obtained from the single-pulse laser-induced decomposition of $(CF_3)_2SiH_2$ (4 kPa, a), CF_3SiH_3 (4 kPa, b), HCF_2SiH_3 (3 and 5.3 kPa (dotted line), c) and H_2CFSiH_3 (4 kPa, d).

irradiation with as many as 10^3 pulses. Above the threshold, an extensive white or yellow chemoluminescence is observed, and the parent compounds are completely or almost completely depleted. Gaseous silicon-containing products (SiF_4 and $SiHF_3$) were the same in all the decomposition processes which were studied, while carbon-containing products (gaseous or solid) differed (Table II; Figure 4). A discussion for individual (fluoromethyl)-silanes, based on data compiled in Table II and Figure 4, is given below.

(Fluoromethyl)silane (I). Irradiation of H_2CFSiH_3 results in the formation of gaseous CH_4 as a major product. Minor amounts of $HSiF_3$, C_2H_2, and SiF_4 are formed together with some solid material deposited on the inside of the reactor.

More than 80% of the silicon of I was exploited in the formation of the deposit, only small quantities of SiF_4 and $HSiF_3$ being formed (Table II). The IR spectrum of the solid is very similar to that of silicon carbide[21] (a broad band between 800 and 900 cm^{-1}; Figure 4d), and it proves the occurrence of some material with many Si–C and some with few Si–H and C–H bonds. The deposit studied by ESCA analysis[22] up to 5-nm depth was revealed to be mostly organosilicon compounds rather than silicon carbide. The deficiency of carbon in the gaseous products (11–61%) is lower than that of silicon (ca. 80%), and it increases with the increasing pressure of I, which, considering the exothermicity of the decomposition process, indicates that more C is used to build up solid material when more heat is released in the irradiated system. The laser Raman spectrum (Figure 5a) shows a broad band with a maximum at ~1500 cm^{-1}, which is typical[23] of amorphous carbon.

(Difluoromethyl)silane (II). The explosive IRMPD of II leads to the same gaseous products as those of I, more C_2H_2 instead of CH_4 being formed and additional minor products, of which one showed a very prominent IR feature near 2080 cm^{-1} (Figure 6). This infrared absorption could not be assigned to any compound known to us. The M^+ $m/e = 74$ peak in the MS spectrum of the decomposition products suggested that $HCCSiH_2F$ might be the unknown species, and we synthesized this compound by mild fluorination of $HCCSiH_2Cl$[24] with SbF_3. However, it showed $\nu_{C\equiv C}$ at 2062 cm^{-1} and, in addition, a strong Q branch of the SiH stretching vibrations at 2221 cm^{-1}, which was absent in the IRMPD decomposition products of II eventually investigated by high-resolution IR spectroscopy.

By prolonged fluorination of $HCCSiH_2Cl$ with $SbCl_3$-doped SbF_3 we finally obtained the yet unknown ethynyltrifluorosilane, $HCCSiF_3$, which showed exactly the same IR band as the unknown species (Figure 6). Thereafter, the identity of the unknown decomposition product was confirmed by a Q branch at 3314 cm^{-1} (ν_{CH}), which both products had in common.

At lower pressures (≤3 kPa), no obvious solid products were visible, and the interior of the reactor appeared clean even after carrying out 10 or more explosive reactions. The determined amounts of gaseous products (Table II) show that carbon and fluorine of II were exploited almost completely for the formation of gaseous compounds, while hydrogen and silicon were lacking in the gaseous products by 14–42 and 40–54%, respectively. Very weak absorption bands at ~650, 840–900, and 2150–2250 cm^{-1}, which persisted when the reactor was evacuated after several experiments, seem to provide a reasonable explanation since they indicate the presence of hydrogenated amorphous silicon.[25-27] They are due to a translucent layer deposited on the reactor windows. The formation of SiF_6^{2-} is confirmed by the IR absorption at 725 cm^{-1} (Figure 4c).

At higher pressures (5.3 kPa), the explosive reaction is accompanied by the formation of a black smog, which deposits only very reluctantly onto the reactor walls. The

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Table II. Products and Material Balance for the Decomposition of (Fluoromethyl)silanes

		gaseous products, kPa					element lacking in volatile products, %			
compd	pressure, kPa	CH_4	C_2H_2	C_2F_4	$HSiF_3$	SiF_4	Si	C	H	F
H_2CFSiH_3 (I)	0.6	0.40	0.07		0.01	0.07	87	11	42	49
	1.1	0.70	0.10		0.05	0.13	83	18	45	35
	2.7	1.20	0.15		0.11	0.29	85	42	60	44
	6.7	2.3	0.15		0.39	>0.40	<88	61	71	59
HCF_2SiH_3 (II)	0.3	0.20	0.03		0.07	0.09	40	5	14	0
	0.5	0.20	0.16		0.11	0.17	48	3	42	5
	0.7	0.40	0.20		0.14	0.21	51	0	27	12
	1.5	0.70	0.40		0.27	>0.3	~54	0	35	18
CF_3SiH_3 (III)	0.7		0.27	trace	0.13	~0.3	~40	20	67	27
	1.3		0.53	0.01	0.15	~0.3	~69	19	69	62
	2.0		0.53		0.33	~0.3	~70	46	77	65
	4.0		0.69	trace	0.47	>0.3		65	85	
$(CF_3)_2SiH_2$ (IV)	0.5		trace	0.01	<0.01	≥0.4	<12	98	94	>44
	0.7		0.1	0.03	0.04	~0.3	<54	96	97	>70
	1.3		trace	0.03	0.11	≥0.5		98	96	
	5.3			<0.01	0.05			~100	~100	>70

IR spectrum of this deposit differs from that obtained at lower pressures (Figure 4c) and shows strong absorptions at ~850 and 940 cm^{-1} along with weaker absorption at 1100, 2150, and 2900 cm^{-1}. The absence of an absorption band due to SiF_6^{2-}, which had been observed in low-pressure experiments, implies that no intermediary HF (see later) is formed. ESCA analysis[22] revealed that the deposit is related to silicon carbide.

(Trifluoromethyl)silane (III). Irradiation of III yields, according to IR and ^{19}F NMR spectra, significant amounts of C_2H_2, SiF_4, and $HSiF_3$ along with traces of C_2F_4 and *cyclo*-C_3F_6. A solid black product is also formed. The material balance (Table II) reveals that Si, C, H, and F originating from III are contained in the gaseous products only in fractional amounts and that their deficiency corresponds to 40–70 (Si), 20–65 (C), 67–85 (H), and 27–65% (F). These deficiencies increase with the increasing pressure of III.

The distribution of all the elements between gaseous and solid products is confirmed by IR spectra. The deposit (Figure 4b) exerts absorption bands in the region of 725 cm^{-1} (SiF_6^{2-}), ~2150 (ν_{Si-H}) and 2950 cm^{-1} (ν_{C-H}), which may suggest the occurrence of a reaction[28] between HF, SiF_4, and NaCl (as in the case of other (fluoromethyl)-silanes) and also the presence of a material composed of C, Si, and H. Broad absorption bands at 910 and 960 cm^{-1} appear to be associated with δ_{SiH_2} of hydrogenated silicon with possible contributions from ν_{Si-F} and/or ν_{Si-C}. But these contributions seem insignificant since the analysis of the deposit by ESCA[22] is in line with the presence of graphitic carbon and the absence of material with Si–C bonds. Any insight gained from laser Raman spectroscopy into the chemical environment of the carbon atoms is precluded owing to a strong luminescence of the surface.

Bis(trifluoromethyl)silane (IV). Irradiation of $(CF_3)_2SiH_2$ results in the formation of SiF_4 and minor amounts of $HSiF_3$ and C_2F_4 accompanied by traces of C_2H_2, copious black material being deposited concomitantly. The material balance for the gas-phase compounds (Table II) and data on the deposit (Figure 4a) show that silicon and fluorine of IV are exploited for the formation of both gaseous and solid products, while carbon is almost completely utilized only for the formation of solid deposits. The IR spectrum of the deposit exhibits only a very weak absorption at 2950 cm^{-1} (ν_{C-H}) and no absorption in the region of ν_{Si-H} vibrations (2100 cm^{-1}), which implies the presence of some C–H but no Si–H groups. A strong absorption band at 725 cm^{-1} belongs to Na_2SiF_6. ESCA analysis of the deposit[22] is supportive of a material containing Si–C bonds, although it shows that the material consists mostly of carbon.

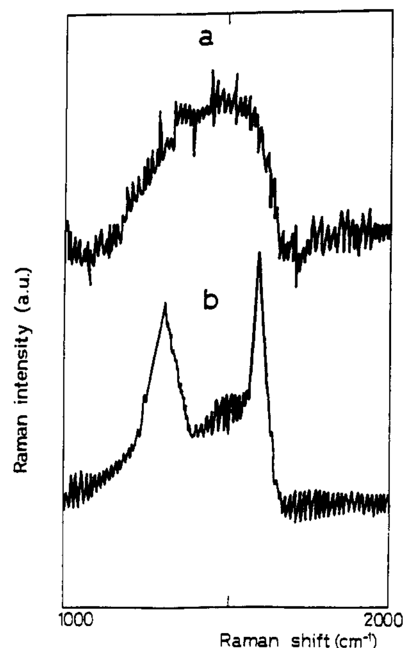

Figure 5. Laser Raman spectra of the deposit from the decomposition of H_2CFSiH_3 (a) and $(CF_3)_2SiH_2$ (b).

The laser Raman spectrum of the deposit (Figure 5b) shows two distinct peaks at 1300 and 1600 cm^{-1}, which can be correlated[29] with the vibrational spectrum of graphite.

Mechanism and Discussion

The gaseous reaction products indicate that fluorine has almost completely migrated from carbon to silicon, the thermodynamically stable fluorosilanes $HSiF_3$ and SiF_4 being formed. Carbon is recovered in the gas phase as CH_4 and the high-temperature species C_2H_2. The fraction of the two later decreases with the increasing fluorine content in the parent molecules, III and IV forming no CH_4 at all (Figure 7). Indeed, only traces of C_2H_2 were detected in the laser-induced decomposition of IV, C_2F_4 formed by dimerization of CF_2 being obtained instead. Presuming that Si is recovered in the gas phase as volatile fluorosilanes, the carbon content of the deposited solid

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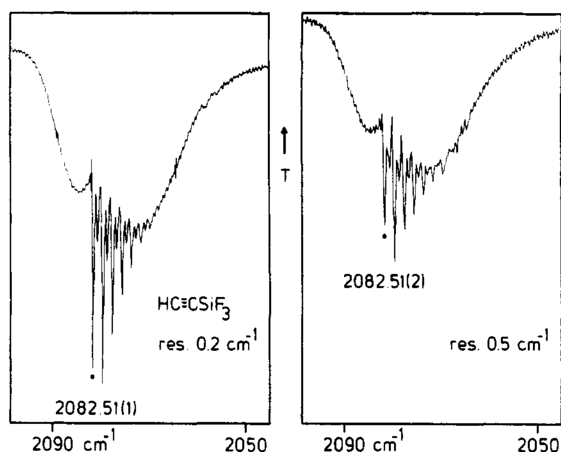


Figure 6. IR spectra in the $\nu(C{\equiv}C)$ region of $HCCSiF_3$ (left) and of the gaseous products produced by IRMPD of II (right).

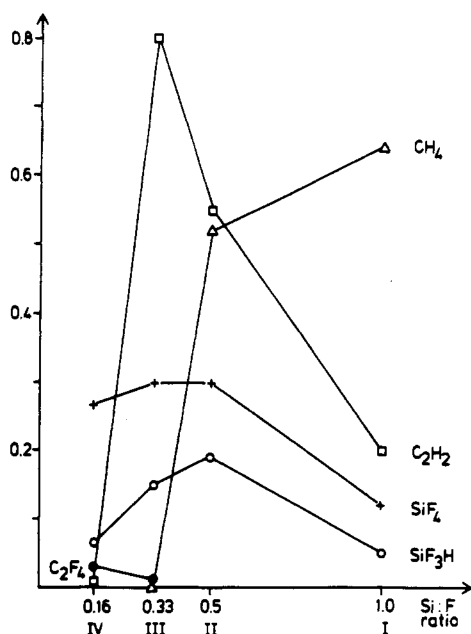
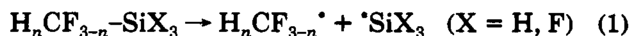


Figure 7. Mole fraction of gaseous products formed by explosive decomposition of (fluoromethyl)silanes I–IV interpolated to ca. 1 kPa.

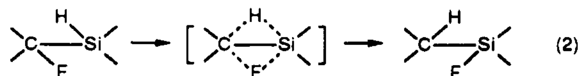
material (the lack of carbon in the gas-phase products) should increase with the fluorine content of the parent molecule. The carbon content in the deposit is however not steadily growing from I to IV but is lowest for II, which indicates that I decomposes by a mechanism different from that operating with II–IV.

Several radical mechanisms or carbene/silylene intermediates can account for the products of the laser-induced decomposition reaction of compounds I–IV. The investigations of the gas-phase thermolysis suggest, however, that α-(fluoromethyl)silanes prefer decomposition channels other than the homogenous cleavage of the Si–C bond (eq 1). The formation by a dyotropic rearrangement of

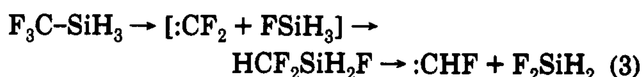


$$H_nCF_{3-n}\text{–}SiX_3 \rightarrow H_nCF_{3-n}^{\bullet} + {}^{\bullet}SiX_3 \quad (X = H, F) \qquad (1)$$

a thermodynamically favored Si–F bond (eq 2) plays a



dominating role in the thermal decomposition of I, while a sequence of carbene elimination and insertion reactions (eq 3) governs the thermolysis of IV and analogously of



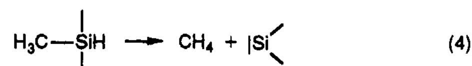
$$F_3C\text{–}SiH_3 \rightarrow [:CF_2 + FSiH_3] \rightarrow HCF_2SiH_2F \rightarrow :CHF + F_2SiH_2 \qquad (3)$$

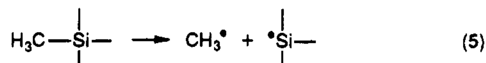
II and III. Both reactions 2 and 3 are exothermic, the sum of the bond energies Si–F + C–H ($\sim$1090 kJ·mol^{-1}) exceeding that of Si–H + C–F ($\sim$830 kJ·mol^{-1}). The $\sim$260 kJ·mol^{-1} net gain may render possible even such unfavorable reactions as homolytic Si–C fission (eq 1).

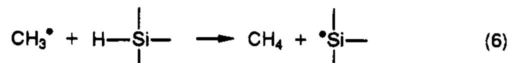
No attention was given to heterogeneous wall effects in the conventional thermolysis of I–IV, while surface-catalyzed processes involving radicals were established for the thermolysis of V.[10] The occurrence of free radicals in the latter process was, however, not confirmed for the homogeneous decomposition in a shock-tube, which yields the same products as the IR laser-induced photolysis.[12]

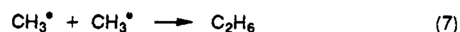
The cascade of the CF/SiH rearrangement reactions (eqs 2 and 3) of I–IV during conventional thermolysis stops when arriving at the thermodynamically favored methylfluorosilanes, but the explosive IR laser-induced decomposition proceeds further to yield CH_4, C_2H_2, and fluorosilanes, along with solid deposits of varying composition.

We propose that CH_4 can be formed by two competing mechanisms (eqs 4–6) involving precursors with CH_3Si









groups. Such methyl silanes are typically formed by a dyotropic rearrangement (eq 2) of H_2CFSi derivatives or, alternatively, by the insertion of CH_2 into the Si–H bonds. The reaction is similar to that of eq 3. No carbene was however detected[20] in the conventional thermolysis of I and II.

The elimination of alkane (eq 4) has been established for the homogeneous decomposition of organosilanes,[11,12,30] and the energetically less favored radical processes (eqs 5 and 6) are at best of minor importance, since C_2H_6, the dimerization product of $CH_3^{\bullet}$, has not been detected in the decomposition products of I and II.

C_2H_2 may be similarly formed via radical or carbene/silylene intermediates. Ethyne is particularly abundant in the thermolysis products of III (Figure 7), where no methane was detected. This indicates that the formation of methylsilane was replaced by more favorable reaction channels. The transformation of CF_3 groups into C_2H_2 requires both a recombination of C_1 units and efficient CF/SiH redistribution reactions. Homolytic Si–C cleavage with subsequent recombination of fluoromethyl radicals (eq 8) to yield the required C_2 units appears to be of minor relevance for the explosive IR photolysis of III–IV, since both fluoroethane (eq 8) and fluoromethane species (eq 9) were absent among the decomposition products.

Contrary to homolytic Si–C cleavage the carbene/silylene mechanism for the IRMPD of I–III offers more favorable pathways to the main product C_2H_2. Elimination

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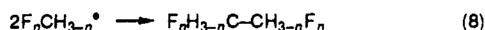
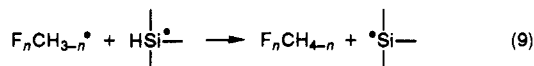


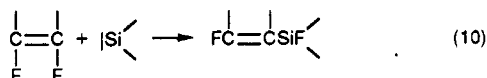
(8)



(9)

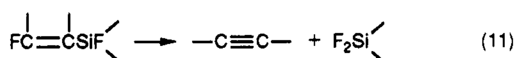
of fluorocarbenes (eq 3) accomplishes both a CF/SiH exchange and formation of C_2 units by dimerization. C_2F_4 obtained from quite inert CF_2 was indeed detected among the products of the explosive decomposition of III and IV.

The formation of silylene by elimination of alkane (eq 4) or H_2 is well documented in homogeneous decompositions of alkyl or hydridosilanes.[12] Reactions of silylenes with alkenes are known to yield vinylsilanes (eq 10).[13,31]



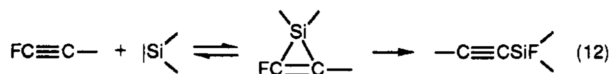
(10)

The formation of SiF bonds should be the driving force for the supposed elimination of ethyne derivatives from fluorovinylsilanes according to (11). Ethyne derivatives

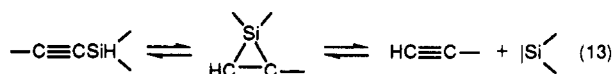


(11)

are known[32-34] as ideal silylene scavengers. Resulting ethynylfluorosilanes (eq 12) were indeed identified among the products of the explosive decomposition of II and III. The equilibria involving ethynylsilanes, silacyclopropenes, and silylenes (eq 13) ensure complete SiF/SiH exchange, with formation of C_2H_2 by irreversible Si–F bond formation.

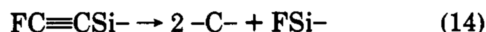


(12)



(13)

Monofluoro-[35] and in particular difluoroethyne,[36] and supposedly fluoroethynylsilanes, are suitable precursors for the deposition of C from the gas phase (eq 14), while silylenes[37] have been employed as precursors for the formation of SiH layers.



$$\mathrm{FC{\equiv}CSi\text{-}} \rightarrow 2\ \mathrm{\text{-}C\text{-}} + \mathrm{FSi\text{-}} \quad (14)$$

Irradiation into the $\delta_s(SiH_3)$ band (944.2 cm^{-1}) of methylsilane (V) performed under similar conditions yields dimethylsilane, methane, hydrogen, and traces of silane and ethene (as observed in the gas-phase thermolysis[10,12]) together with a solid deposit containing Si–C, C–H, and Si–H bonds.[38] The decomposition is not explosive, and it can be driven at 1–2 kPa to about 15% conversion with a few tens of high fluence (1 J·cm^{-2}) pulses. Interestingly, a pulse of 0.8 J·cm^{-2} fluence in an effective volume of 7 cm^3 causes an energy uptake of 216 kJ·mol^{-1}, which corresponds to almost 20 photons absorbed by one molecule of V, and the absorbed energy roughly equals the energy barrier for a molecular three-center decomposition (260 kJ·mol^{-1}).[10] Although this number of photons is about three times higher than in the case of (fluoromethyl)silanes (Table III), no explosive decomposition is induced and V is depleted only to a very low extent. These results support the availability of a low-energy channel when the α-carbon of methylsilane is bonded to a F atom.

Table III. Laser Absorption Parameters of (Fluoromethyl)silanes

compd	irradiating wavenumber, cm^{-1}	effective abs cross section,[a] 10^{-20} cm^2	energy absorbed in effective vol,[b] kJ $mole^{-1}$	no. of photons absorbed/molecule[b]
H_2CFSiH_3	927.0	10.5	77	6.9
HCF_2SiH_3	1025.3	12.3	65	5.3
CF_3SiH_3	916.6	7.2	51	4.6
$(CF_3)_2SiH_2$	922.9	4.4	42	3.8

[a] At 0.7 kPa and fluence of 0.3 J·cm^{-2}. [b] At 1.3 kPa and fluence much below the explosion limit; effective volume is given by the sizes of the beam and path length.

The formation of some Na_2SiF_6 accounts only for small amounts of any intermediary HF. The energy released in the decomposition of I–IV grows with increasing pressure of the parent compound and the progress of the reaction, which is due to the high exothermicity of the CF/SiH rearrangement. It may be responsible for the complete decomposition of hot products originating from radical recombinations. The visible luminescence, observed during the explosions, indicates that some decomposition routes can also be induced from electronically excited species.

We note that the explosive IRMPD of fluoromethylsilanes can be induced with significantly less energy fluence compared to laser driven reactions in mixtures of silane SiH_4 and hexafluorobenzene[28] or hexafluoroacetone,[17,39] which yield similar solid products. These observations can be rationalized in terms of the collisional energy pooling process during the IRMPD of (fluoromethyl)silanes (Table III), which contrasts with the energy transfer from a vibrationally excited, activated molecule to a cold (nonabsorbing) collisional partner in bimolecular laser-induced reactions. A very weak absorption band near 1100 cm^{-1} (Figure 4) observed in the IR spectra of the deposits immediately after the explosion and evacuation of the reactor can be attributed to a $\nu_{as}(SiOSi)$ vibration known to possess extremely high molar absorptivity. Compounds with an Si–O–Si linkage can also arise from reactions with traces of water inevitably present on NaCl windows of the reactor. We note that the deposited samples were exposed to the atmosphere prior to ESCA analysis and therefore their oxygen content is sufficiently large to imply that the materials are reactive toward oxygen and that they form Si–O or C–O bonds.

Although the main aim of the present study was the investigation of gaseous products formed in the IRMPD of (fluoromethyl)silanes, we can conclude that the process involving the C → Si fluorine shift and Si–C bond cleavage is unsuitable for the production of (FSi, CH) deposits.

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