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Gas-Phase Homolytic Substitution Reactions of Hydrogen Atoms at Silicon Centers

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The reaction of H atoms with a number of mono-, di-, and trisilanes has been studied with the view of examining the possible occurrence of a homolytic substitution reaction (S_H2). Arrhenius parameters for abstraction plus substitution have been determined for the reaction of H atoms with Si_2H_6, $Me_3SiSiMe_2H$, $Me_3SiSiCl_3$, Si_2Cl_6, and Me_8Si_3. The ratio of substitution vs. abstraction was determined. It is found that di- and trisilanes react fast by an S_H2 reaction while monosilanes are unreactive. Ligands with a -I effect cause a decrease in reactivity. The experimental facts are explained by a frontside attack of the H atoms due to the favorable interaction of the singly occupied orbital at the H atom with the energetically high-lying Si-Si orbital.

Introduction

Homolytic substitution reactions (S_H2), i.e., second-order reactions between an incoming free radical and a substrate molecule to give a product molecule and a leaving radical, at polyvalent centers have been extensively studied in the liquid phase.[1] It is found that S_H2 reactions at second-row elements, with the exception of boron, are very rare. In the few cases where such a reaction has been observed at a carbon[2,3] or oxygen[4] center, it was found to proceed in a synchronous manner with inversion of configuration. The much greater ease with which S_H2 reactions occur at boron or higher row elements indicates that this is due to the availability of a low-lying unoccupied orbital at the reaction center for the incoming radical. In some cases a two-step mechanism, radical addition followed by elimination, has indeed been found to occur.[5]

Reports on S_H2 reactions at a polyvalent center in the gas phase are much less abundant. This is, no doubt, due to the small number of studies on compounds containing higher row elements. Only in hot atom chemistry are S_H2 reactions quite common, even at a carbon center.[6] Experiment[6] and theory[7] are in agreement as to the high activation energies for such reactions. S_H2 reactions with reagents at thermal energies were again found with boron,[8] sulfur,[9] and organometallic compounds.[10]

Substitution reactions at a silicon center have been observed by Band and Davidson[11] and by Strausz and coworkers[12] in the reaction of iodine and hydrogen atoms, respectively, with disilanes. Bell and Platt[13] also reported indications of a substitution reaction of CF_3 radicals with tetramethylsilane. We have found that H atoms react with hexamethyldisilane exclusively by a substitution reaction,[14] and we have also determined the Arrhenius parameters for this reaction.[15] It turned out that the reaction of hydrogen atoms with hexamethyldisilane yielding trimethylsilane and trimethylsilyl radicals had Arrhenius parameters similar to those of hydrogen abstraction reactions from the Si-H bond in monosilanes. The question was now raised as to why substitution reactions are not observed with monosilanes, at least not with H atoms as reactant, but are so facile in the case of disilanes. One possible reason given was the smaller bond dissociation energy between leaving group and silicon center in the case of disilanes.[15]

To gain further information on the factors influencing homolytic substitution reactions we studied the reaction of H atoms with a number of mono-, di-, and trisilanes.

Results

Si_2H_6. Two primary processes have been identified in the reaction of H atoms with disilane:[12,16] substitution

$$H + Si_2H_6 \rightarrow SiH_4 + SiH_3 \tag{1a}$$

and abstraction

$$H + Si_2H_6 \rightarrow H_2 + Si_2H_5 \tag{1b}$$

We have determined the second-order overall rate constant $k(1)$ for processes 1a and 1b with the pulse photolysis-resonance absorption method. Figure 1 shows the Ly-α light intensity as a function of time. The pseudo-first-order rate constants, $k^1(1) = -[H]^{-1}(d[H]/dt)$ derived from such measurements, showed a dependence on the initial hydrogen atom concentration. From Figure 2 one can derive two limiting values for $k^1(1)$ for low and high mercury light intensities, respectively. The dependence of these two limiting rate constants on the Si_2H_6 concentration is shown in Figure 3. We consider the smaller bimolecular rate constant to be the correct one despite the larger difference with the recommended literature value.[17] The temperature dependence of $k(1)$ (Figure 4) was measured at an initial hydrogen atom concentration of 3.8×10^{12} cm^{-3}. From the room-temperature value of $k(1)$ and its tem-

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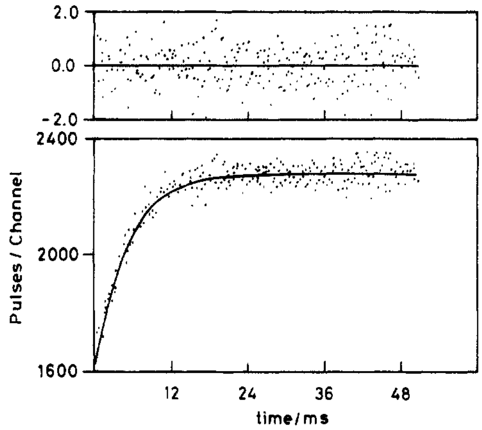

Figure 1. Dependence of the transmitted Ly-α intensity (counts/channel) as a function of time. The solid line refers to a nonlinear least-squares fit involving three adjustable parameters, one of which is the pseudo-first-order rate constant $k^1(1)$. The upper part of the figure shows weighted residuals.

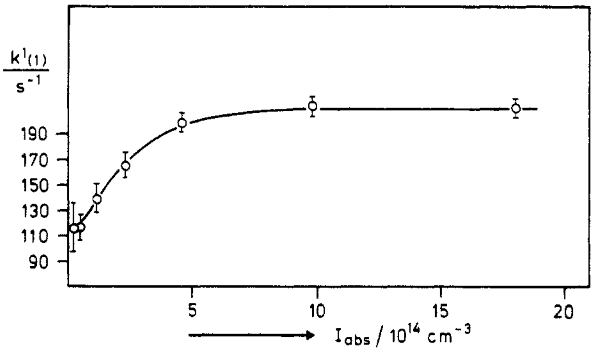

Figure 2. Dependence of the pseudo-first-order rate constant $k^1(1)$ on the absorbed intensity of the mercury resonance radiation.

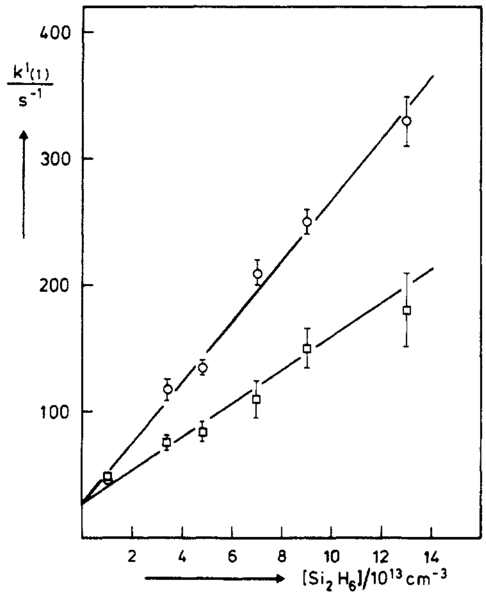

Figure 3. Dependence of the extrapolated zero intensity pseudo-first-order rate constant (□) and of the limiting high intensity rate constant (○) on disilane concentration.

perature dependence the following numerical Arrhenius expression for $k(1)$ is obtained

$$k(1) = (4.2 \pm 1.8) \times 10^{10} \exp\left(-\frac{9.6 \pm 0.8}{RT}\right) \mathrm{M^{-1}\ s^{-1}}$$

where the activation energy is given in kJ mol^{-1}. No curvature in the Arrhenius plot (Figure 4) was detected within the temperature range employed.

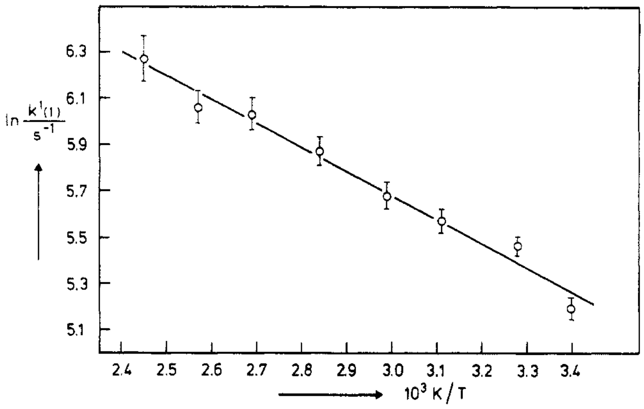

Figure 4. Arrhenius plot for $k^1(1)$.

By stationary photolyses we tried to determine the ratio $k(1a)/k(1b)$ by measuring the product ratio SiH_3D/HD in the system $Hg/D_2/Si_2H_6$. The values obtained had a wide scatter, mainly due to the HD content of D_2. We obtained $k(1a)/k(1b) \approx |SiH_3D|/|HD| = 0.19 \pm 0.12$. The complementary system $Hg/H_2/Si_2D_6$ yielded a more accurate value: $k(1a)/k(1b) \approx |SiD_3H|/|HD| = 0.27 \pm 0.04$.

$(CH_3)_3SiSi(CH_3)_2H$. An unexpected large rate constant for process 2 was found at room temperature, $k(2) = (6.0 \pm 0.3) \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$. With this value and its temperature

$$\mathrm{H + Me_3SiSiMe_2H \rightarrow products} \qquad (2)$$

dependence we obtained the following expression

$$k(2) = (1.6 \pm 0.4) \times 10^{10} \exp\left(-\frac{8.0 \pm 0.4}{RT}\right) \mathrm{M^{-1}\ s^{-1}}$$

The ratio of substitution vs. abstraction $(k(2a) + k(2b))/k(2c)$ was again determined in two ways: static mercury-sensitized photolysis of D_2 in the presence of pentamethyldisilane and mercury-sensitized decomposition of neat pentamethyldisilane yielding H atoms and the pentamethylsilyl radical (eq 2a–c).

$$\mathrm{H + Me_3SiSiMe_2H \rightarrow Me_3SiH + Me_2SiH\cdot} \qquad (2a)$$

$$\mathrm{H + Me_3SiSiMe_2H \rightarrow Me_2SiH_2 + Me_3Si\cdot} \qquad (2b)$$

$$\mathrm{H + Me_3SiSiMe_2H \rightarrow H_2 + Me_3SiSiMe_2\cdot} \qquad (2c)$$

In the case of mercury-sensitized photolysis of D_2 only moderate accuracy was achieved for the same reasons as given above. Assuming that $Me_2SiH\cdot$ and $Me_3Si\cdot$ do not react to give Me_2SiH_2 and Me_3SiH, respectively (see below), we obtained

$$\frac{k(2a) + k(2b)}{k(2c)} \approx \frac{|\mathrm{Me_3SiD}| + |\mathrm{Me_2SiDH}|}{|\mathrm{HD}|} = 0.12 \pm 0.03$$

while the second system yielded

$$\frac{k(2a) + k(2b)}{k(2c)} \approx \frac{|\mathrm{Me_3SiH}| + |\mathrm{Me_2SiH}|}{|\mathrm{H_2}|} = 0.164 \pm 0.016$$

For the ratio of the two substitution channels we obtained

$$k(2a)/k(2b) \approx |\mathrm{Me_3SiH}|/|\mathrm{Me_2SiH_2}| = 0.90 \pm 0.17$$

a mean value from both systems.

Apart from Me_3SiH, Me_2SiH_2, and H_2, also $Me_3SiSiMe_2SiMe_2H$, Me_8Si_3, and $n\text{-}Me_{10}Si_4$ were identified. These products can be easily accounted for in terms of the products of combination reactions of the radicals formed in the primary processes (eq 3–5). Product ratios

$$\mathrm{2Me_3SiSiMe_2\cdot \rightarrow \mathit{n}\text{-}Me_{10}Si_4} \qquad (3)$$

$$\mathrm{Me_3Si\cdot + Me_3SiSiMe_2\cdot \rightarrow Me_8Si_3} \qquad (4)$$

$$\mathrm{Me_2SiH\cdot + Me_3SiSiMe_2\cdot \rightarrow Me_7Si_3H} \qquad (5)$$

found $(|Me_2SiH_2| + |Me_3SiH|)/(|Me_8Si_3| + |Me_7Si_3H|) = 2.1 \pm 0.7$ and $|H_2|/(2|Me_{10}Si_4| + |Me_8Si_3| + |Me_7Si_3H|) = 3.5 \pm 1.0$ are quite different from the value of 1 required by the mechanism. There are at least two reasons for this discrepancy: first, other recombination reactions, (6), (7), and (8), should also occur. These however escaped detection since their products either are identical with the substrate (eq 8) or as impurities present in the substrate at 0.4% (eq 6) and 0.3% (eq 7). Second in addition to reactions 3–8 the radicals may lead to disproportionation reactions to an extent as yet unknown. If these reactions were to lead to Me_2SiH_2 and/or Me_3SiH to an appreciable extent, a different ratio of substitution vs. abstraction would result. In any case the numbers given above for this ratio are only upper limits. For the ratio $|Me_8Si_3|/|Me_7Si_3H|$ a value of 1.4 ± 0.1 was found.

$$2Me_3Si\cdot \rightarrow Me_6Si_2 \quad (6)$$

$$2Me_2SiH\cdot \rightarrow Me_4Si_2H_2 \quad (7)$$

$$Me_3Si\cdot + Me_2SiH\cdot \rightarrow Me_5Si_2H \quad (8)$$

$(CH_3)_3SiSiCl_3$. Replacement of three methyl groups in hexamethyldisilane by chlorine results in a substantial decrease of the rate constant for reaction 9

$$H + Me_3SiSiCl_3 \rightarrow \text{products} \quad (9)$$

as compared to reaction 10[15]

$$H + Me_3SiSiMe_3 \rightarrow Me_3SiH + Me_3Si\cdot \quad (10)$$

This reduction is exclusively due to a smaller *A* factor.

$$k(9) = (2.7 \pm 2.6) \times 10^9 \exp\left(-\frac{14.8 \pm 1.7}{RT}\right) M^{-1}\ s^{-1}$$

$$k(10) = (7.8 \pm 1.8) \times 10^9 \exp\left(-\frac{14.7 \pm 0.4}{RT}\right) M^{-1}\ s^{-1}$$

The product spectrum of the static photolysis at room temperature reveals only substitution reactions (9a) and (9b) with $k(9a)/k(9b) = |Cl_3SiH|/|Me_3SiH| = 4.3 \pm 1.5$.

$$H + Cl_3SiSiMe_3 \rightarrow Cl_3SiH + Me_3Si\cdot \quad (9a)$$

$$H + Cl_3SiSiMe_3 \rightarrow Me_3SiH + Cl_3Si\cdot \quad (9b)$$

Si_2Cl_6. The rate of disappearance of H atoms in the presence of Si_2Cl_6 was rather small and at the maximum substrate pressures attainable in our experiments, barely discernible. We can only give an upper limit to the rate constant at room temperature for reaction 11 $k(11) \leq 1.8 \times 10^6\ M^{-1}\ s^{-1}$. Measurements at higher temperatures were very imprecise as well ($E_A/R = 1600 \pm 200$ K). It cannot be excluded that the observed rate is due to impurities. If the observed rate is really due to a reaction with Si_2Cl_6, then for energetic reasons reaction 11 can only be a substitution reaction leading to Cl_3SiH and $Cl_3Si\cdot$. Search for Cl_3SiH by GC, MS, and IR in steadily illuminated samples did not provide any evidence for its presence. In the case of mass spectrometric product analysis, 1% Cl_3SiH in Si_2Cl_6 could have been detected.

$$H + Si_2Cl_6 \rightarrow \text{products} \quad (11)$$

Table I. Summary of the Experimental Data

	$(k' + k'')/10^6$ $M^{-1}\ s^{-1}$	k'/k''	$DH^0(Si–X)/$ $kJmol^{-1\ b}$	IP/eV^c
Si_2H_6	180		309	10.5
$Me_3SiSiMe_2H$	96	0.9	330	
$Me_3SiSiMe_3$	21		334	8.7
$Cl_3SiSiMe_3$	7	4.3	351	
$Cl_3SiSiCl_3$	<2		343	10.9
Me_3SiCMe_3	...		318	
$Me_3SiCH_2SiMe_3$	...		351	
$Me_3SiSiMe_2SiMe_3$	78	0.3		

[a] k' and k'' are room-temperature rate constants for substitution reactions at the first and second silicon center, respectively. [b] For X = Si or C, values are calculated from data given in ref 19 and 20. [c] Vertical ionization potential as measured by PES.

$(CH_3)_3SiSi(CH_3)_2Si(CH_3)_3$. In the reaction of H atoms with octamethyltrisilane the following three products were observed with the mole fractions in parentheses: Me_3SiH (0.2), $Me_3SiSiMe_2H$ (0.6), and $Me_3SiSiMe_3$ (0.2). At higher conversion (≥3%) $Me_3Si(SiMe_2)_2SiMe_3$ was also observed. Formation of these products can be understood in terms of a simplified mechanism, in which all disproportionation reactions are neglected (eq 12–14). From a product analysis we estimate

$$H + Me_3Si_8 \rightarrow Me_3SiSiMe_2H + Me_3Si\cdot \quad (12a)$$

$$H + Me_3Si_8 \rightarrow Me_3SiH + Me_3SiSiMe_2\cdot \quad (12b)$$

$$2Me_3Si\cdot \rightarrow Me_3SiSiMe_3 \quad (13)$$

$$2Me_3SiSiMe_2\cdot \rightarrow Me_3Si(SiMe_2)_2SiMe_3 \quad (14)$$

$$k(12a)/k(12b) \approx |Me_3SiSiMe_2H|/|Me_3SiH| = 3.0 \pm 0.5$$

The rate constant for processes 12a and 12b is given by

$$k(12) = (7.2 \pm 4.2) \times 10^9 \exp\left(-\frac{11.0 \pm 0.1}{RT}\right) M^{-1}\ s^{-1}$$

$(CH_3)_3CSi(CH_3)_3$. This system was studied only by steady-state photolysis at room temperature. Neither Me_3SiH nor Me_3CH was detected.

$(CH_3)_3SiCH_2Si(CH_3)_3$. No substitution products such as trimethylsilane were formed in room-temperature steady-state photolysis.

Cl_2CCCl_2. This system was only studied by the pulse photolysis–resonance absorption method in the temperature range 290–500 K. No reaction has been detected in agreement with a previous study.[18] Only an upper limit of $k(H + C_2Cl_4) \leq 3 \times 10^6\ M^{-1}\ s^{-1}$ at 500 K can be given.

Discussion

Our experimental data together with other relevant parameters are summarized in Table I. Even though only qualitative trends in rate constants and Arrhenius parameters are called upon for the elucidation of the substitution mechanism, it should be mentioned that quantitative agreement with pertinent literature data[17] is poor. Only the system H/Si_2H_6 has been studied before by other authors. The groups of Strausz[12] as well as of Lampe[21] have determined the room-temperature rate constant $k(1)$ relative to that for H atom addition to C_2H_4. Both groups find higher values. We attribute this discrepancy, at least in part, to too large a rate constant for the system H/C_2H_4.[22] For the ratio $k(1a)/k(1b)$ a value of 0.52 has been reported.[12] This value is appreciably higher than our values and even more so if one takes isotope effects into account. From our data we expect a value for $k(1a)/k(1b)$ for H + Si_2H_6 close to 0.2.

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For a homolytic substitution, located between a nucleophilic and an electrophilic substitution reaction, two extreme models may be envisaged: (i) backward attack with synchronous formation and breaking of the two bonds involved; (ii) addition of the radical to the reaction center followed by bond breaking of the leaving group. Case i is commonly encountered in substitution reactions at a monovalent center, usually proceeding with low activation energy. Simple three center models like the BEBO.[23,24] method give already a good description of such processes but fail completely to account for substitution reactions at a polyvalent center which, as in the case of carbon, proceed with high activation energy. With boron and higher row elements mechanism ii should gain in importance due to the availability of low-lying unoccupied orbitals.[1]

In reactions of Si compounds the participation of d orbitals has frequently been invoked.[25] In the reaction of H atoms with monosilanes the intermediate existence of a pentavalent silicon was postulated by different groups,[26-29] but experimental or theoretical support for this hypothesis could not be provided.[30-33] Assuming that the availability of d orbitals is a requirement for the substitution reaction to occur, it is quite surprising how fast these reactions proceed with some of the disilanes (Table I). One explanation offered in an earlier publication[15] is the smaller Si–Si bond dissociation energy as compared to the H-, CH_3-, and Cl-substituted monosilanes so far studied. Consulting Table I one observes indeed a decrease of the room-temperature rate constant with increasing SiSi bond dissociation energy, but already Si_2Cl_6 does not fit into this correlation and the nonoccurrence of a substitution reaction in the case of *tert*-butyltrimethylsilane with its low Si–C bond dissociation energy suggests quite clearly that the bond energy between the silicon center and the leaving group is not a crucial factor. Neither H atoms nor other radicals studied so far undergo a substitution reaction with monosilanes, in agreement with liquid-phase studies.[34] We therefore have to conclude that at least for H atoms the presence of two Si atoms adjacent to each other is essential for the occurrence of a fast substitution reaction, and not the availability of empty d orbitals at one silicon center.

Disilanes are distinguished from monosilanes by their high-lying Si–Si bonding orbital,[35] well separated from the other σ orbitals. Furthermore, in polysilanes these SiSi orbitals can interact with each other, allowing electron delocalization as in conjugated alkenes.[35]

This suggests that the first step of the substitution reaction can be regarded as an addition of H atoms to the Si–Si bond. And indeed, there are striking similarities between a substitution reaction at a silicon center, adjacent to another silicon atom, and H atom addition to a C=C double bond:

The activation energies for the substitution reactions in disilanes are very low, quite comparable to the value for H atom addition to ethylene.[36] The *A* factors are smaller by an order of magnitude, indicating that the transition state is tighter than in the case of alkenes. We therefore expect a dependence of the substitution rate constant on the Si–Si as well as on the newly formed Si–H bond strength. The dependence on the Si–Si bond energy has already been noted. The strong reduction of the reactivity in the case of chlorine-substituted disilanes has its exact counterpart in the alkene series. Finally, the pronounced greater reactivity of octamethyltrisilane in comparison to hexamethyldisilane resembles the increased reactivity of conjugated π systems toward hydrogen atoms.

The similarity of the reactivity of a Si—Si σ bond with a C=C π bond has also been noted in the reaction of O atoms with hexamethyldisilane which proceeds by insertion of the O atom into the Si—Si bond.[37]

The similarity between substitution and addition reaction should also manifest itself in a similarity of the transition states. We therefore suggest that the substitution reaction starts with a frontside attack of the hydrogen atom on the Si–Si bond with concomitant elongation of the latter.

One is led to similar conclusions by the frontier orbital theory.[38] Within this model the interaction between H atom and disilane is reduced to an interaction between the singly occupied molecular orbital (SOMO) of the H atom and LUMO and/or HOMO of the disilane. The HOMO is the energetically high-lying Si–Si σ orbital ($\epsilon_{HOMO} \approx -10$ eV), a hybrid orbital with presumably predominant p, less s, and very little d orbital contributions.[39] The energetic position of the Si–Si σ orbital is very similar to the π orbitals in alkenes. The energetic position of the LUMO can be estimated from a relation given by Houk[40] to be $\epsilon_{LUMO} \approx +1$ eV. The high ionization potential of the H atom argues in favor of a SOMO-HOMO interaction, in agreement with the electrophilic character of the H atom.[38]

The interaction between SOMO and HOMO will lead to frontside attack and not to an S_N2-type reaction with inversion of configuration due to the greater localization of the Si–Si σ orbital between the two Si centers. Furthermore, the interaction between SOMO and HOMO will become appreciable already at large distances due to the diffuseness of the Si–Si bonding orbital. The experiments with pentamethyldisilane and 1,1,1-trichloro-2,2,2-trimethyldisilane provide data in support of the model. Backside attack of the H atoms at pentamethyldisilane along the molecular axis will occur with approximately the same probability from either side. While at the $(CH_3)_3Si$ side only substitution can take place, there is a strong competing reaction, namely, abstraction, if the reaction proceeds from the $(CH_3)_2HSi$ side. Therefore we would expect a ratio $|(CH_3)_2SiH_2|/|(CH_3)_3SiH| << 1$ and not the experimentally observed value of about one. On the other hand, a ratio of about one is expected in the case of a

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frontside attack. Backside attack at the trimethyltrichlorodisilane should lead preferentially to trimethylsilane; however, the observed predominant formation of trichlorosilane can only be explained by a frontside displacement.

In the case of molecules with two Si–Si σ bonds one expects the highest electron density at the middle Si atom. The preferred formation of pentamethyldisilane is in agreement with this expectation.

Chlorine ligands exert two effects on the energetic position of the adjacent orbital. The conjugative effect shifts the orbital to higher and the inductive effect to lower energies. The former effect predominates in the case of alkenes,[41] and the latter in the case of disilanes. In both cases the reactivity toward H atoms is found to be dramatically reduced, indicating that small changes in the orbital energy are not responsible. It is considered likely that shielding of the reaction site is effected by the nonbonding orbitals of the chlorines. The inductive effect will probably lead to a reduction of the diffuseness of the Si—Si σ and C=C π orbitals, thereby decreasing the interaction of SOMO and HOMO at the site of the transition state. The greater compactness of the Si—C orbital is probably also an element in the nonoccurrence of the substitution reaction in the case of Me_3CSiMe_3 and $Me_3SiCH_2SiMe_3$.

Conclusion

Homolytic substitution at silicon by H atoms proceeds fast if at least one second Si atom is bonded to the substitution center. This is explained by the favorable interaction of the SOMO at the H atom and the Si–Si bonding orbital of the disilane. Ligands with an –I effect lead to a decrease in reactivity. This model also suggests that the substitution reaction proceeds by a frontside attack of the H atom accompanied by a synchronous breaking of the Si–Si bond. Similar conclusions have been drawn by Strausz et al.[42] from kinetic isotope effects.

Experimental Section

Methods. Absolute rate constants and their temperature dependences were measured by a pulse photolysis–resonance absorption method. The apparatus has been described in recent publications,[15,43] and only a short description will be given here. The hydrogen atoms were generated by mercury-sensitized photolysis of H_2. The light of a DC low-pressure mercury resonance lamp (Gräntzel, Typ5) was pulsed by a combination of a moderately slow (3 ms) mechanical shutter (Compur 3) and fast (10 μs) electrical switching of the lamp. The pulse length could be continuously varied between 70 μs and steady illumination. Pulse frequencies used in this study were in the range of 1–0.1 s^{-1}. The absorbed light intensity of the unattenuated mercury resonance radiation was measured by propane actinometry,[44] $I_{abs} = 1.8 \times 10^{15}$ cm^{-3} s^{-1}; this means that at the shortest pulse length the initial hydrogen concentration amounted to 2.5×10^{11} cm^{-3}. The gases, (1–1.2) × 10^5 Pa of He with 133 Pa of H_2 or alternatively (1–1.2) × 10^5 Pa of pure H_2, and 1–10 Pa of substrate were premixed in a 20-L vessel and then pumped through a thermostated mercury reservoir and through the reaction chamber. The pressure in the cell (6.65×10^4 Pa) was kept constant by means of an automatic pressure controller (MKS 250 A). H atoms were detected by means of a sensitive resonance lamp (DC discharge in He). After the light was passed through the reaction chamber, the radiation was dispersed by a 0.5-m VUV monochromator (McPherson 235) and detected by a solar blind photomultiplier (EMR-614 G). The inhomogeneous generation of H atoms noted in an earlier publication[15] has been practically eliminated by using a reaction cell with a small optical path length (1 cm) for the mercury resonance radiation.

All rate constant measurements were carried out in the pseudo-first-order regime. As in the case of H + $Me_3SiSiMe_3$[15] it turned out that the pseudo-first-order rate constants were dependent on the initial hydrogen atom concentration. We interpret this as being due to the reaction of H atoms with radicals formed in the primary step. These processes will die out for very small initial hydrogen atom concentrations.[15] All the room-temperature rate constants reported in this work are values extrapolated to zero mercury light intensity. The temperature dependence (290–500K) of the rate constants were measured at a fixed light intensity.[45]

Stationary photolyses were carried out in 200-cm^3 cylindrical quartz cells with a low-pressure mercury resonance lamp (Gräntzel, Typ 5), thermostated, and flushed with N_2 to ensure a constant light output. The light was partially collimated with a quartz condensor, the absorbed intensity amounted to $I_{abs} = 5 \times 10^{12}$ cm^{-3} s^{-1}. Typical reaction mixtures consisted of 270 Pa of substrate, 2.7×10^4 Pa of H_2, and 0.2 Pa of Hg. Reaction products were analyzed by mass spectrometry (MAT-311 A) and by gas chromatography (Carlo Erba 2900). For organosilanes a 50-m glass capillary column OV 1, FID, and for chlorosilanes a 3-m stainless-steel column, packed with Chromosorb W, HWD, were used. Photochemical conversions were in the range of 1–5%. Ionization potentials were measured by using a Perkin-Elmer PS18 photoelectron spectrometer.

Substances. D_2 (99.7% isotopic purity), He (99.96%), H_2 (99.999%), Si_2Cl_6, and C_2Cl_4 were of commercial origin. Disilanes,[46] Si_2H_6 and Si_2D_6, pentamethyldisilane,[47] 1,1,1-trichloro-2,2,2-trimethyldisilane,[48] *tert*-butyltrimethylsilane,[49] bis(trimethylsilyl)methane[50] and octamethyltrisilane[51] were prepared as described in the literature. D_2 was used without further purification, and He and H_2 were passed through molecular sieves which were cooled by liquid nitrogen. C_2Cl_4 had a gas chromatographic purity of better than 99.99%, and Si_2Cl_6 was distilled by means of a concentric tube column. Disilanes were distilled on a high vacuum line prior to use. All other substances were purified by preparative GC.

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Registry No. Si_2H_6, 1590-87-0; $(CH_3)_3SiSi(CH_3)_2H$, 812-15-7; $(CH_3)_3SiSiCl_3$, 18026-87-4; Si_2Cl_6, 13465-77-5; $(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$, 3704-44-7; $(CH_3)_3CSi(CH_3)_3$, 5037-65-0; $(CH_3)_3SiCH_2Si(CH_3)_3$, 2117-28-4; Cl_2CCCl_2, 127-18-4; $Me_3SiSiMe_3$, 1450-14-2; $Cl_3SiSiCl_3$, 13465-77-5; $Me_3SiCh_2SiMe_3$, 2117-28-4.

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