The Mercury $6(^3P_1)$ Photosensitization of the Methylsilanes and Silane

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The reactions of Hg $6(^3P_1)$ atoms with $MeSiH_3$, Me_2SiH_2, Me_3SiH, Me_4Si, Me_2SiF_2, and $MeSiD_3$ have all been found to involve exclusive initial loss of an H atom from the Si–H bond, if available; otherwise, C–H scission occurs. The quenching cross-section values for the substrates support the kinetic data in that the quenching efficiency of the Si–H bond is much greater than that of the C–H bond. The primary products are H_2, at a quantum yield (Φ) of 0.7–1.0, and the disilane, formed by the recombination of two silyl radicals. Disproportionation of $MeSiH_2$ and Me_2SiH radicals to a minor extent to yield silene radicals and the silane cannot be ruled out. Each substrate was studied as a function of pressure and exposure time. Plots of $\Phi(H_2)^{-1}$ vs. P^{-1} showed a linear relation. Addition of small amounts of NO to the $MeSiH_3$, Me_2SiH_2, and Me_3SiH systems resulted in the complete suppression of disilane formation and the simultaneous appearance of the corresponding disiloxane via a chain mechanism. Temperatures up to 400° had no effect on the Φ-values of the Me_3SiH reaction. Thus the Me_3Si radical is stable up to 400°. However, rising temperatures did increase the amount of alkylsilyl radical ($Me_2HSiCH_2\cdot$) formation. Temperatures up to 200° had no effect on the products or Φ-values in the Me_2SiH_2 reaction. The SiD_4 reaction appears to be surface sensitive, yielding $\Phi(D_2)$ values up to 10. The probable primary $\Phi(D_2)$ is ca. 3.

Introduction

The photochemical kinetics of silicon compounds is virtually a virgin domain. Thus, in the relatively few photochemical studies published in this field, emphasis has been on the synthetic rather than on the kinetic mechanistic aspects of the reactions. Thermochemical data concerning silicon compounds are sparse; bond-dissociation energy values are not well established, and activation energies for free-radical reactions are a rarity indeed. The majority of photolytic studies have been restricted to the halogen derivatives of silane. Only three mercury photosensitization studies have been published,[1-3] all being concerned with the silane molecule, SiH_4. The most recent, by Niki and Mains[3] (which appeared in the literature while the present investigation was in progress), indicated several primary steps for the decomposition, involving silyl and silene (SiH_2) radicals and/or atomic silicon, as well as atomic and molecular hydrogen. The combined contributions of the proposed primary steps gave a $\Phi(H_2)$ value of 1.8, without invoking a chain-propagating step. The other products were an SiH_x polymer, and

di-, tri-, tetra-, and pentasilane, in decreasing order of importance.

The present study was conducted to satisfy a two-fold interest, namely, to obtain some basic information on the chemistry of silicon-containing free radicals and to extend knowledge of the general nature of the energy-transfer mechanisms and primary processes in mercury sensitization.

Experimental

Standard high vacuum techniques were employed throughout. Quantitative studies were performed under static conditions, while the SiD_4 studies and some exploratory experiments were carried out in a circulatory apparatus. In the NO reactions a fast single-pass system was used in order to collect sufficient amounts of the siloxane product for analysis. All apparatus was stopcock grease-free, being equipped either with mercury float valves, Hoke TY440 valves, or Springham Viton stopcocks.

In the main series of quantitative runs, three cylindrical quartz reaction cells were used with dimensions (length by diameter) of 100 × 50, 60 × 50, and 50 × 50 mm. In some experiments, the reaction system was immersed in a constant temperature water bath to obtain higher pressures of the substrate.

The light source was a Hanovia No. 687A45 mercury resonance lamp with neutral density filters for attenuation of the incident intensities. A constant voltage, Sola, CVS transformer was used to stabilize the energy input. Lamp intensities were determined by propane actinometry.[4] Sufficient time was allowed for equilibration with mercury vapor as well as for lamp warm-up. Absorbed light intensities of 0.072–0.133 × 10⁻⁶ einstein/min. were employed.

Materials. Me_4Si (Stauffer) was purified by low temperature distillation at −95° and degassed at −130°. Me_3SiH (Procurement) was first purified by preparative gas chromatography (g.c.) on an 8-ft., medium-activity silica gel column with temperature programming, and then subjected to low temperature distillation at −110° and degassing at −139°. The $MeSiH_3$, Me_2SiH_2, and Me_2SiF_2 (all Peninsular) were distilled at temperatures of −139, −123, and −95° and degassed at −160, −139, and −130°, respectively. CH_3SiD_3 (Merck) was purified in a manner identical with that described for $MeSiH_3$. The extent of deuteration could not be precisely determined, but was estimated to be not better than ca. 96%. SiD_4 (Merck) was distilled at −186° and degassed at −196°. It contained considerable amounts of isotopic impurities. The SiD_4 was distilled prior to each run. The NO purification is described elsewhere.[5] Other materials

(1) H. J. Emeleus and K. Stewart, *Trans. Faraday Soc.*, 32, 1577 (1936).
(2) D. White and E. G. Rochow, *J. Am. Chem. Soc.*, 76, 3897 (1954).
(3) H. Niki and G. J. Mains, *J. Phys. Chem.*, 68, 304 (1964).
(4) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, 19, 319 (1951).
(5) O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, 60, 347 (1963).

were generally of the best available grade and were carefully purified prior to use.

Each of the substituted silanes, even after the most careful purification, contained trace amounts of impurities. These could be removed by pre-irradiation. The pre-irradiations, at the highest feasible pressures, were done repeatedly for 3 to 5 hr. until very pure substrates were obtained.

After each exposure noncondensable fractions were collected at either -196 or $-214°$ and subsequently analyzed by g.c. on a molecular sieves column with He as carrier. A second fraction in the substituted silane systems, distilling at $-160°$, was taken several times during the initial stages of the study of each substrate. This was analyzed by g.c. using a silica gel column.

The final heavy fraction was obtained by distilling at the same temperature as was used in purifying the substrate (see above). The bulk of this fraction was the disilane although it also contained trisilane and presumably other polysilanes. The disilane from each of the substrates had sufficient vapor pressure at room temperature to be measured volumetrically. In the case of the disilane of Me_4Si, use was made of a calibrated bulb attached to a wide bore manometer, the pressure difference being measured with a cathetometer to ±0.01 mm. The composition and purity of this fraction was determined by g.c. with a column packed with DC Silicone Oil 200 on Chromosorb W. This procedure was also employed to obtain pure samples of disilanes and trisilanes for characterization. The heavy condensable fraction from the NO–silane reactions was analyzed on a 20-ft. dimethyl sulfolane column.

Standard methods (g.c., retention times, and mass, infrared, and n.m.r. spectra) were used for identification and structure determination of the disilanes, disiloxanes, and trisilanes. It should be mentioned that the isotopic composition of silicon provides a useful guide for analyzing the mass spectra of disilanes since the three consecutive peaks for the parent molecule, or of a given fragment containing two silicon atoms, appear in the approximate ratio of $13:2:1$ (according to increasing mass).

Results

The mercury sensitization of each of the six substituted silanes yielded only hydrogen in the fraction not condensable at $-196°$. In no instance was a fraction obtained at $-160°$; that is, C_2H_6, C_2H_4, etc., were not formed.

In addition to hydrogen, each of the substrates yielded a disilane, resulting from the combination reaction of two alkylsilyl or silalkyl free radicals, as the only other major reaction product. A trisilane was also isolated from the reactions of $MeSiH_3$, $MeSiD_3$, and Me_3SiH. Trisilanes were probably formed in the Me_4Si and Me_2SiF_2 reactions as well, but could not be isolated and identified by the analytical procedure employed. There was also evidence for the formation of higher polysilanes with four or more silicon atoms. Liquid or solid films (depending on the substrate) were deposited on the cell walls during experiments with long exposure times.

Each system was studied as a function of substrate pressure and exposure time. Me_3SiH and Me_2SiH_2 were also studied as a function of reaction temperature.

A study of secondary reactions was also made by determining the relative yields of disilane and trisilane in the decomposition of Me_3SiH, Me_2SiH_2, and $MeSiH_3$. This was done as a function of substrate pressure and exposure time. Relative disilane to trisilane ratios were obtained from g.c. peak areas.

Tetramethylsilane. The only products found in this system were H_2 and 2,2,5,5-tetramethyl-2,5-disilahexane, $(Me_3SiCH_2)_2$. The mass spectrum of the latter product compared very well with the one reported in the literature.[6]

Φ *vs.* substrate pressure data for the above two products are given in Figure 1. For comparison, the corresponding values for the paraffin analog neopentane are also shown.[7] To obtain sufficiently high Me_4Si pressures, the temperature of the system was increased from 26 to 50° in the plateau region of the curve. This, however, had no observable effect on the reaction. The sixfold increase in mercury vapor concentration in this temperature interval did not affect the product yields, indicating complete absorption of the incident radiation even at the lower temperature.

The results of a time study on the product yields are shown in Figure 2. $\Phi(H_2)$ and $\Phi((Me_3SiCH_2)_2)$ extrapolate to the same limiting value of 0.84 mole/einstein at zero exposure time. With increasing duration of exposure, through secondary decomposition to higher polysilanes, the disilane yield drops more rapidly than the H_2 yield.

Trimethylsilane. The major products of this system are H_2 and 2,2,3,3-tetramethyl-2,3-disilabutane, $(Me_3Si)_2$. This latter product was identified by its g.c. retention time and mass spectrum against an authentic sample. In addition to H_2 and $(Me_3Si)_2$, a third product also appeared in quantities of ca. 0.5%. In mass spectrometric analysis it displayed a parent peak at 146 (and a peak at 145 corresponding to loss of an H atom from the lone SiH bond); consequently, it was tentatively identified as the isomeric product, Me_3Si–CH_2–$SiHMe_2$. This isomer increased in importance with rising temperature, as will be shown below. Quantum yield data for the product formation as a function of substrate pressure and exposure time are presented in Figures 3 and 4. The initial deviation of the Φ(dimer) curve from the $\Phi(H_2)$ curve in the Φ *vs.* P plot (Figure 3) and the convergence with increasing pressure is characteristic of the mono-, di-, and trimethylsilane systems. The exposure time (Figure 4) has little effect on product yields. The extrapolated quantum yield values are $\Phi(H_2) = 0.80$ and $\Phi(Me_3Si)_2 = 0.78$. The mass imbalance, while slight here, becomes more pronounced in the Me_2SiH_2 and $MeSiH_3$ systems.

Small quantities of a trisilane were also isolated from the reaction products by g.c. and examined by mass spectrometry. The parent mass was 218 indicating likely the trisilane structure, Me_3Si–$SiMe_2$–CH_2–$SiMe_3$. The mass spectrum was consistent with the presence of an (–Si–Si–C–Si–) bond system. The trisilane/disilane ratio in the products is shown as a

(6) G. Fritz, H. Buhl, J. Grobe, F. Aulinger, and W. Reering, *Z. anorg. allgem. Chem.*, 312, 201 (1961).
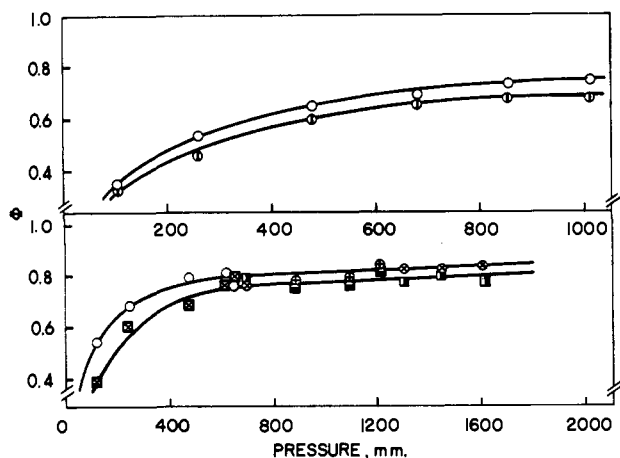(7) R. J. Norstrom, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, 42, 2140 (1964).

Figure 1. Product quantum yields, Φ, *vs.* substrate pressure in the Hg 6(^{3}P₁) sensitized reaction of tetramethylsilane, Me₄Si, and neopentane, Me₄C. Me₄C reaction (upper diagram): H₂ at 26° (O); dineopentyl at 26° (◑). Me₄Si reaction (lower diagram): H₂ at 26° (O), at 41° (⊕), and at 50° (⊗); (Me₃SiCH₂)₂ at 26° (⊠), at 41° (▬), and at 50° (◘▬).
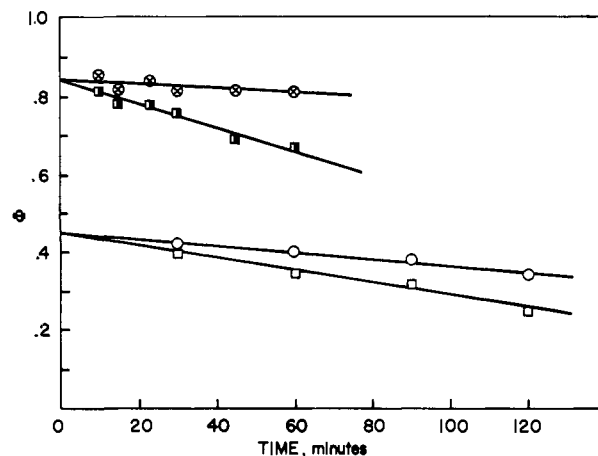

Figure 2. Product quantum yields, Φ, *vs.* exposure time in the Hg 6(^{3}P₁) sensitized reaction of Me₄Si (at 1300 mm.) and Me₂SiF₂ (at 1190 mm.). Me₄Si reaction (upper set): H₂ at 50° (⊗); (Me₃-SiCH₂)₂ at 50° (◻▬). Me₂SiF₂ reaction (lower set): H₂ at 26° (O); (MeSiF₂CH₂)₂ at 26° (◻).

function of substrate pressure in Figure 5, and of exposure duration in Figure 6. The trends are as expected for a secondary product.

Dimethylsilane. Quantum yield data for the two major reaction products, H₂ and 2,3-dimethyl-2,3-disilabutane, (Me₂SiH)₂, are given as a function of pressure and exposure duration in Figures 3 and 4, respectively. The only other product detected was the trisilane, C₆H₂₀Si₃.

The mass, infrared, and n.m.r. spectra of the dimer product were obtained from the isolated g.c. effluent. The mass spectrum showed an intense parent peak at 118. However, the largest peak was at mass 59 (Me₂SiH⁺), with strong responses appearing for fragments of mass 117, 103, 102, 73, and 58. In the infrared spectrum, strong absorption maxima appeared at frequencies corresponding to CH₃, Si–H, Si–C, Si–CH₃, and Si–Si. The n.m.r. spectrum in CS₂ showed a septet and a doublet centered on τ-values of 6.28 (A) and 9.86 (B), respectively; the integrated areas were in the ratio of 1:6, as expected for the Si–H (A) and methyl (B) protons in the molecule (CH₃)₂SiHSiH(CH₃)₂, which appears to be the only dimer present.

From Figure 4 the extrapolated quantum yield values are: Φ(H₂) = 0.81 and Φ((Me₂SiH)₂) = 0.71. The deviation between the two quantum yield values here is more pronounced than in the previous two systems described above, but it appears to decrease with increasing substrate pressure.

The trisilane product of the present system, C₆H₂₀Si₃, for which the yields related to dimer are shown in Figures 5 and 6, was isolated by g.c. and examined by mass spectrometry. A parent peak of mass 176 was obtained. A reasonable structure of this compound would be Me₂SiH–SiMe₂–SiMe₂H, derived from an SiH bond split in (Me₂SiH)₂ and the recombination of the resulting radical with the Me₂SiH radical, or from the recombination of a Me₂Si biradical with two Me₂SiH radicals.

Dimethyldifluorosilane. The two products isolated and identified were H₂ and 2,2,5,5-tetrafluoro-2,5-disilahexane, (MeF₂SiCH₂)₂. The latter was identified

by mass spectral analysis of a sample obtained from the g.c. effluent. A weak parent peak of 190 was obtained along with a cracking pattern, the major fragments of which corresponded to masses 175, 109, 90, 98, 81 (the largest), 63, 62, and 47. Although SiF₄ and CH₃F were specifically sought their presence could not be detected.

The quantum yield data for products formation as a function of substrate pressure and exposure duration are given in Figures 7 and 2, respectively. The steadily rising Φ-values with pressure up to 1700 mm. indicate a low quenching efficiency of this molecule for Hg 6(^{3}P₁) atoms (Table IV). The Φ *vs.* exposure time plots in Figure 2 are qualitatively similar to those found in the Me₄Si reaction. The Φ-values of the two products, H₂ and disilane, are nearly equal (0.45 and 0.44, respectively) at a substrate pressure of 1190 mm.

The data in Figure 7 require further explanation. The upper sections of the plots were obtained at a temperature of 37° to extend the substrate pressure range. The resulting slight increase in Φ may indicate a small activation energy for the quenching reaction.

Methylsilane. The two major products were H₂ and 2,3-disilabutane, (MeSiH₂)₂. The latter was isolated by g.c. and identified by its infrared, n.m.r., and mass spectra. The mass spectrum showed an intense parent peak at 90 and strong responses for the fragments of mass values 89, 88, 87, 86, 85, 75, 74, and 45 (the largest). The infrared spectrum showed the same absorption as the (Me₂SiH)₂, except that the intensities differed owing to differences in the number of CH₃ and SiH groups in the two compounds.

The n.m.r. spectrum displayed a quartet and a triplet centered on τ-values of 6.42 (SiH) and 9.76 (CH), respectively. The integrated peak areas, CH₃/SiH, were in the ratio of 1.5 as required for the MeSiH₂–SiH₂Me structure. Silicon isotope satellites were in the expected proportions. In spin decoupling, the quartet collapsed to a singlet with the silicon isotopic satellites again in the correct ratio. Similar results were obtained for the quartet. As in the case of (Me₂SiH)₂, there was no evidence of compounds with methylene hydrogens in the disilane fraction.
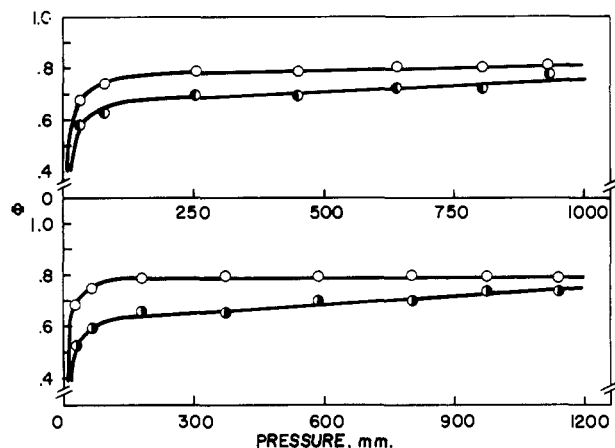
Figure 3. Product quantum yields, Φ, vs. substrate pressure in the Hg $6(^3P_1)$ sensitized reaction of Me_3SiH and Me_2SiH_2. Me_3-SiH reaction (upper diagram): H_2 at $26°$ (O); $(Me_3Si)_2$ + traces of $Me_3SiCH_2Si(Me)_2H$ (◑). Me_2SiH_2 reaction (lower diagram): H_2 at $26°$ (O); $(Me_2SiH)_2$ (◐).
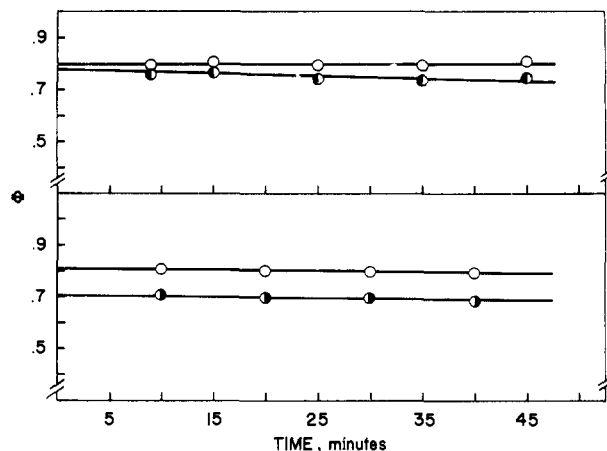

Figure 4. Quantum yield vs. exposure time for the Hg $6(^3P_1)$ sensitized reaction of Me_3SiH (at 960 mm.) and Me_2SiH_2 (at 800 mm.). Me_3SiH reaction (upper diagram): H_2 at $26°$ (O); $(Me_3-Si)_2$ + traces of $Me_3SiCH_2SiMe_2H$ (◑). Me_2SiH_2 reaction (lower diagram): H_2 at $26°$ (O); $(Me_2SiH)_2$ (◐).

Quantum yields for H_2 and dimer, as a function of substrate pressure and exposure time, are shown, respectively, in Figures 8 and 9.

The trisilane $C_3H_{14}Si_3$ was identified by mass spectrometry. A parent peak was obtained at mass 134. From the fragments showing in the spectrum it would appear that the trisilane contains the –Si–Si–Si– linkage. Relative yields of $(MeSiH_2)_2$ and $C_3H_{14}Si_3$ are plotted as a function of substrate pressure and exposure time in Figures 5 and 6, respectively. Whereas $MeSiH_3$ might be expected to give the highest trimer/dimer ratios of the series, in fact, it gives values which fall between those obtained for Me_2SiH_2 and Me_3SiH. Since the $\Phi(H_2)$ values of all three substrates are identical, the higher ratios for the $MeSiH_3$ reaction must be due to a more rapid loss of trisilane than obtains in the Me_2SiH_2 reaction.

Methylsilane-d_3, MeSiD$_3$. This compound was studied to determine the H/D isotope effect on the reaction. The reaction products of this system were the deuterated counterparts of those obtained in the Me-SiH$_3$ reaction. The noncondensable fraction at $-196°$ contained 93.6% D_2, 4.9% HD, and 1.5% H_2. Since the deuteration of the substrate molecule was estimated to be not higher than *ca.* 96%, both the primary step as well as the subsequent H-atom abstraction reaction would appear to yield the CH_3SiD_2 radical exclusively. This was further supported by the mass spectrometric analysis of the disilane, $(CH_3SiD_2)_2$, and trisilane products.

The quantum yield data for the formation of products as a function of substrate pressure and exposure time are given in Figures 8 and 9. It will be noted from Figure 9 that varying the exposure time has little effect on $\Phi(D_2)$, and that the apparent mass balance at zero exposure time is better than for the $MeSiH_3$ reaction. On the other hand, $\Phi(D_2)$ is somewhat lower at 0.71 compared to the $\Phi(H_2)$ value of 0.80 for $MeSiH_3$. All of these effects can presumably be attributed to the higher Si–D bond energy.

Perdeuteriosilane, SiD$_4$. The reaction products of this system were D_2, Si_2D_6, Si_3D_8, Si_4D_{10}, and a solid polymer, which became a visible deposit only on prolonged irradiation. The quantum yield data for product formation are tabulated in Table I. The salient features of this reaction may be summarized as follows.

(a) The $\Phi(D_2)$ values exceed unity, in agreement with the recent findings of Niki and Mains,[3] who reported

Table I. The Hg $6(^3P_1)$ Sensitized Reaction of SiD_4[a]

Run no.	Exposure time, min.	P (SiD_4), mm.	Moles/einstein		Remarks
			$\Phi(D_2)$	$\Phi(cond.)$[b]	
41	5	60	6.1	0.70	Clean cell
38	10	11	1.7	0.29	
39	10	50	2.4	0.56	
35	10	66	1.9	0.78	
40	5	60	3.1	0.63	
43	5	60	8.1	1.4	Clean cell
44	5	60	3.5	0.68	
45	5	60	3.6	0.70	
46	5	60	3.1	0.80	
47	5	60	3.5	0.65	
48	2	60	9.9	0.91	Clean cell
49	2	60	7.1	0.67	
50	2	60	4.9	...	
51	2	58	9.6	1.0	Clean cell
52	2	58	5.6	0.61	
53	2	58	4.3	0.52	
54	2	58	3.7	0.48	
55	2	58	3.4	...	
56	2	58	3.4	0.42	
57	2	58	3.4	0.42	
11–12	30	200	3	0.7	

17–19 $P(SiD_4) = 30$ mm.; $P(C_2H_4) = 60$ mm.
The main product in the condensable fraction was $D_3Si-CH_2-CH_2D$
Total yield of hydrogen from the reaction $= 1.84 \times 10^{-6}$ mole
Yield of hydrogen from the decomposition of $SiD_4 = 1.43 \times 10^{-6}$ mole
Yield of hydrogen which should have been obtained from the SiD_4 on competitive quenching basis $= 2.10 \times 10^{-6}$ mole
Scavenging by $C_2H_4 = (0.7/2.1)100 = 33\%$

[a] Runs between lines are comparable. [b] Condensable at $-160°$. Mass spectrometric and g.c. analysis indicated the presence of Si_2D_6, Si_3D_8, and Si_4D_{10} in this fraction, in the g.c. peak area ratio of $82:4:1$.
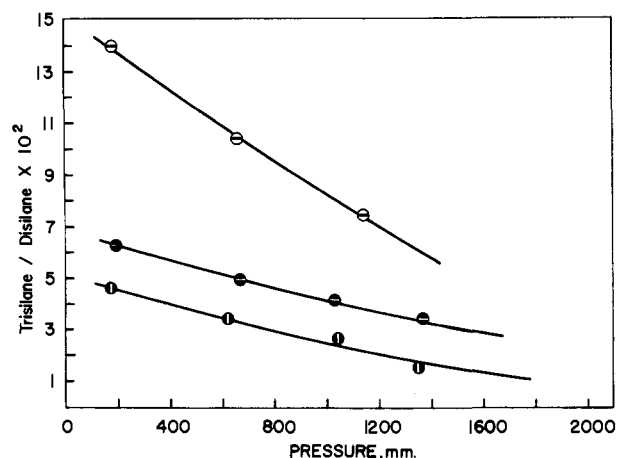
Figure 5. Relative trisilane/disilane yields as a function of substrate pressure in the Hg 6($^3P_1$) sensitized reaction of Me$_3$SiH, Me$_2$SiH$_2$, and MeSiH$_3$: Me$_3$SiH reaction for 150-min. runs (⬤); Me$_2$SiH$_2$ reaction for 60-min. runs (⊖); MeSiH$_3$ reaction for 60-min. runs (◗).
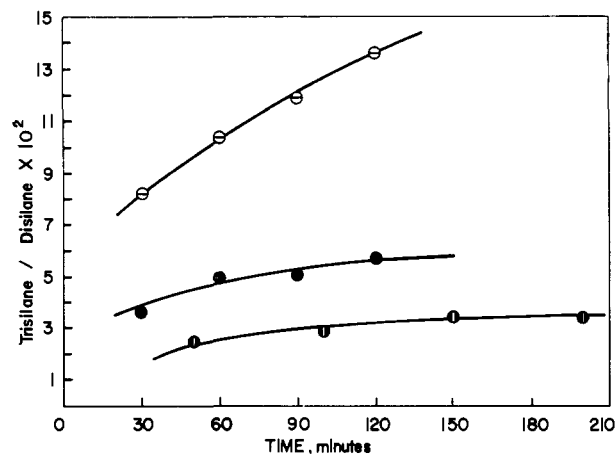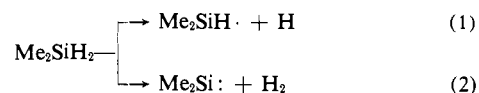

Figure 6. Relative trisilane/disilane yields as a function of exposure time in the Hg 6($^3P_1$) sensitized reaction of Me$_3$SiH, Me$_2$SiH$_2$, and MeSiH$_3$: Me$_3$SiH reaction at 620 mm. (◗); Me$_2$SiH$_2$ reaction at 656 mm. (⊖); MeSiH$_3$ reaction at 664 mm. (⬤).

a $\Phi(H_2)$ value of 1.8 at 10 mm. substrate pressure and small conversion.

(b) More significantly the $\Phi(D_2)$ values obtained here appear to be strongly surface dependent. In a clean cell, at low conversions, $\Phi(D_2)$ attained ca. 10. In consecutive runs, performed without cleaning the reaction cell, $\Phi(D_2)$ declined and seemed to level off at values of ca. 3–3.5.

(c) $\Phi(cond.)$ is considerably less than $\Phi(D_2)$, indicating that polymer formation is due to primary reaction fragments.

(d) From runs on SiD$_4$, admixed with C$_2$H$_4$ to trap D atoms, it appears that a considerable fraction of the primary deuterium product is D$_2$.

Reactions in the Presence of Added Nitric Oxide. The reactions were markedly altered upon addition of small amounts of NO. The formation of di- and polysilanes was completely suppressed. In addition to H$_2$, whose yield increased considerably, N$_2$ and a disiloxane containing the primary radical appeared as principal products. The data obtained from the MeSiH$_3$–NO systems in the circulatory apparatus are given in Table II. It is evident from the yields of all the major products that a chain mechanism is operative. SiD$_4$ behaves somewhat differently from MeSiH$_3$ in that N$_2$O is an important product in its reaction. It is also to be noted from the data that N$_2$ and H$_2$ formation does

Table II. The Mercury Sensitization of MeSiH$_3$ and SiD$_4$ in the Presence of NO

P (NO), mm.	Moles/einstein					
	$\Phi(H_2)$	$\Phi(N_2)$	$\Phi(N_2O)$	$\Phi(cond.)$	$\Phi(CH_4)$	$\Phi(C_2H_4)$
	P(MeSiH$_3$) ~ 700 mm.					
0	0.8	...	...	0.6	...	...
1.0	2.26	1.80	0.10	1.78	0.10	0.33
7.6	3.61	2.05	0.46	1.61	0.20	0.73
15	2.32	2.10	0.45	1.94	0.44	0.31
54	2.83	2.86	0.71	2.36	1.13	0.17
40[a]	10.5	4.44	...	...	...	...
	P(SiD$_4$) = 45 mm.					
0	3	...	...	0.7	...	...
3.0	2.58	1.16	2.64	0.85	...	...

[a] The reaction mixture was left to stand 18 hr. between completion of the irradiation and analysis.

not cease immediately at the end of irradiation, although there is no evidence for dark reaction. This implies the presence of long-lived reactive intermediates in the reacting system.

The MeSiH$_3$–NO, Me$_2$SiH$_2$–NO, and Me$_3$SiH–NO mixtures were also run in a fast-flow, single-pass apparatus which permitted collection of sufficient amounts of material, for g.c., STPV–molecular weight determination, and mass, infrared, and n.m.r. spectroscopic identification of the siloxane product against authentic samples. From g.c. analysis the condensable fraction contained ca. 80 peak-area % disiloxane and the rest higher molecular weight material. For MeSiH$_3$–NO mixtures, this latter product appeared to have molecular weight of 240, tentatively corresponding to (MeSiH$_2$)$_4$·(NO)$_2$.

Temperature Studies. In an effort to obtain information about the thermal stability of free silyl radicals, a brief temperature study of the Me$_2$SiH$_2$ and Me$_3$SiH reactions was made. No data were available on the thermal stability of the parent compounds themselves. However, related members have been reported[8] to be stable up to 1000°. A study has also been reported[9] on the thermal isomerization of the disilane (Me$_3$Si)$_2$ to Me$_2$SiH–CH$_2$–SiMe$_3$, which begins at 600°.

The results obtained on the Me$_2$SiH$_2$ system are shown in Figure 10. The salient features are as follows: $\Phi(H_2)$ and the nature of products remain unchanged up to ca. 200°. Pyrolysis, which is probably of a heterogeneous nature, begins at ca. 200°. At 276° pyrolysis is considerably more rapid than decomposition by irradiation. In addition to (Me$_2$SiH)$_2$, four other products appear at this temperature; the former accounts for about 75% of the total. Neither CH$_4$ nor C$_2$H$_6$ is formed. It is estimated, that ca. 90% of the thermolysis proceeds either by eq. 1 or 2 or both, followed by

$$\text{Me}_2\text{SiH}_2 \begin{cases} \longrightarrow \text{Me}_2\text{SiH·} + \text{H} & (1) \\ \longrightarrow \text{Me}_2\text{Si:} + \text{H}_2 & (2) \end{cases}$$

radical recombination or insertion processes.

(8) A. D. Petrov, G. J. Danilova-Dobryakova, and F. Trokhova, *Zh. Obshch. Khim.*, 30, 235 (1961); *J. Gen. Chem. USSR*, 30, 252 (1961).

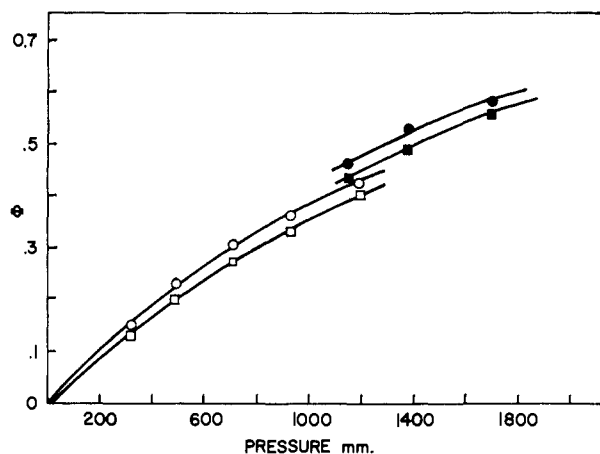(9) K. Shiina and M. Kumadu, *J. Org. Chem.*, 23, 139 (1958).

Figure 7. Quantum yield *vs.* substrate pressure for the Hg $6(^3P_1)$ sensitized reaction of Me_2SiF_2: H_2 at 26° (○) and at 37° (●); $(MeSiF_2CH_2)_2$ at 26° (□) and at 37° (■).

Figure 8. Quantum yield *vs.* substrate pressure for the Hg $6(^3P_1)$ sensitized reaction of $MeSiH_3$ and $MeSiD_3$. $MeSiD_3$ reaction (upper diagram): D_2 at 26° (◎); $(MeSiD_2)_2$ (◐). $MeSiH_3$ reaction (lower diagram): H_2 at 26° (○); $(MeSiH_2)_2$ (◐).

The results for the Me_3SiH reaction are given in Table III. This substrate also has no temperature coefficient for the primary process, as is evident from the

Table III. The Hg $6(^3P_1)$ Sensitized Decomposition of Trimethylsilane as a Function of Reaction Temperature[a]

Temp., °C.	Exposure time, min.	$R(H_2)$, μmoles/60 min.	G.c. peak area/60 min.		Isomer, %
			$R((Me_3-Si)_2)$	$R(Me_2-SiHCH_2-SiMe_3)$	
25	60	2.51	1900	...	0.6
136	60	2.49	1948	10	0.5
245	60	2.49	1847	68	3.6
346	60	2.44	1742	190	9.8
400	60	2.53	1562	346	18.1
400[b]	0	0.05	...	...	...
400	30	2.52	1740	258	13.0
400	60	2.53	1562	346	18.1
400	90	2.46	1488	406	21.4
400[c]	90	2.56	1572	428	21.4
400	120	2.67	1562	535	25.5

[a] $P(Me_3SiH) = 130$ mm.; $I_a = 0.0719 \times 10^{-6}$ einstein/min. [b] Blank, no irradiation. [c] After the lamp was shut off, the substrates and products were kept in the cell for an additional 90 min. at 400°.

relatively constant hydrogen yields up to 400°, where thermal decomposition begins to take place. Again neither CH_4 nor C_2H_6 was formed. The condensable fraction was composed of $(Me_3Si)_2$, trisilane, and the isomer $Me_2SiH-CH_2-SiMe_3$. It can be seen from the data, that while the sum of the two disilanes (based on g.c. areas) are constant in the whole temperature interval, the yield of the isomer increases with temperature. This increase, in part, may be due to the increasing importance of the C–H *vs.* Si–H bond cleavage in the primary process (*vide infra*). The time study carried out at 400° indicated a strong dependence of the isomeric product yields on exposure time, which appears to be due to the secondary Hg $6(^3P_1)$ sensitized isomerization of $(Me_3Si)_2$ to $Me_2SiH-CH_2-SiMe_3$.

Discussion

From the facts (a) that in the reactions with Hg $6(^3P_1)$ atoms (Hg*) of each of the six substituted silanes examined, the only two primary products detected
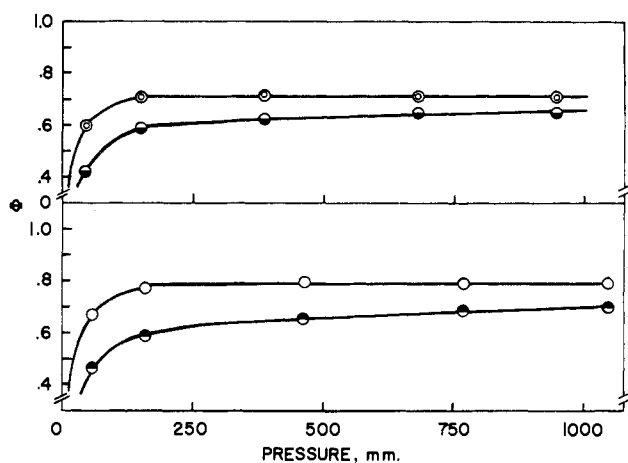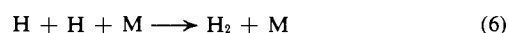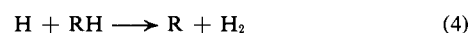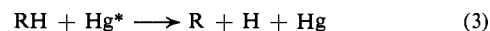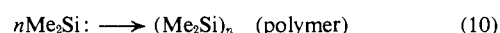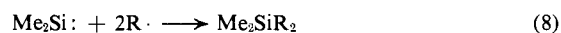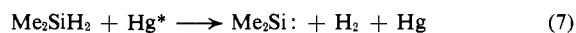
were H_2 and the corresponding disilane in equal or nearly equal yields, and (b) that nitric oxide in quantities of less than 1% completely suppresses disilane formation with the simultaneous appearance of disiloxanes in which the primary silyl radical structure is retained, the following simple sequence is indicated.

$$RH + Hg^* \longrightarrow R + H + Hg \qquad (3)$$
$$H + RH \longrightarrow R + H_2 \qquad (4)$$
$$R + R \longrightarrow R_2 \qquad (5)$$
$$H + H + M \longrightarrow H_2 + M \qquad (6)$$

In the case of mono- and dimethylsilanes—where a significant mass imbalance exists in the α *vs.* time relations (*cf.* Figures 4 and 9) even at zero exposure time—processes of secondary importance such as

$$Me_2SiH_2 + Hg^* \longrightarrow Me_2Si: + H_2 + Hg \qquad (7)$$
$$Me_2Si: + 2R \cdot \longrightarrow Me_2SiR_2 \qquad (8)$$
$$Me_2Si: + Me_2SiH_2 \longrightarrow Me_2SiH-SiHMe_2 \quad \text{(insertion)} \qquad (9)$$
$$nMe_2Si: \longrightarrow (Me_2Si)_n \quad \text{(polymer)} \qquad (10)$$

cannot be ruled out, especially so, since primary elimination of H_2, as in eq. 7, has been invoked[3] for the SiH_4 reaction, and insertion reactions like eq. 9 have been postulated[10] for the dimethylsilene biradical, Me_2Si.

Disregarding step 7, the primary cleavage in the substituted silanes (eq. 3) resembles that of the analogous carbon compounds, the paraffins; thus, in both systems only H atoms are removed. From the nature of the disilane products it follows that step 3 involves Si–H scission exclusively when such bonds are available; otherwise C–H scission occurs (*e.g.*, Me_4Si and Me_2SiF_2). The analogy between substituted silanes and hydrocarbons may best be seen from a comparison of Me_4Si with Me_4C, where radical disproportionation reactions are absent for structural reasons. The nature of the products, the quantum yield values ($\Phi(H_2)_\infty = 0.88$ for both systems), and the kinetics of the reactions are quite similar (*cf.* Figure 1). When primary or secondary alkyl radicals are involved, the reaction becomes more complicated owing to their dispropor-

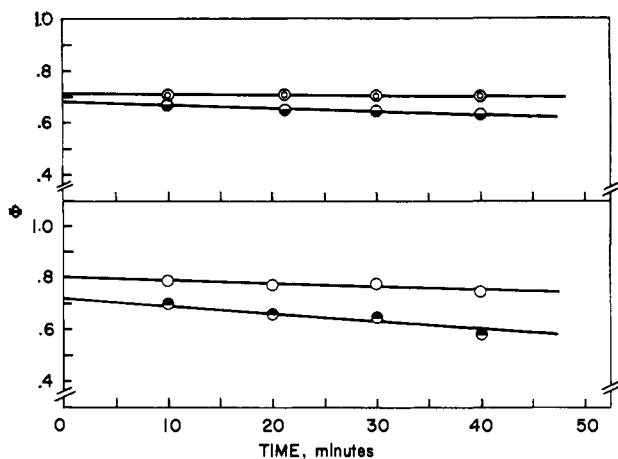(10) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

Figure 9. Quantum yield vs. exposure time in the Hg 6(^{3}P$_1$) sensitized reaction of MeSiH$_3$ (at 1049 mm.) and MeSiD$_3$ (at 945 mm.). MeSiD$_3$ reaction (upper diagram): D$_2$ (◎); (MeSiD$_2$)$_2$ (◐). MeSiH$_3$ reaction (lower diagram): H$_2$ (O); (MeSiH$_2$)$_2$ (●).

Figure 10. Total H$_2$ yield vs. reaction temperatures in the Hg 6(^{3}P$_1$) sensitized reaction of Me$_2$SiH$_2$ for 30-min. runs at 210 mm. The yield of 6.41 $\times$ 10^{-6} mole at 276° is almost entirely from thermal reaction.

tionation reactions. Since silyl or substituted-silyl radicals do not form olefin-type compounds,[11] it is usually assumed that they do not disproportionate. The inability of Si atoms to form a π-bond with Si or C atoms is generally attributed to inner-shell repulsions and the relatively poor overlap between 3p and 2p, or 3p and 3p π-orbitals. This, however, would not preclude the possibility of disproportionation reactions leading to biradical formation, such as

$$SiH_3 + SiH_3 \longrightarrow 2SiH_2: + H_2 \qquad (11)$$

$$R_2SiH + R_2SiH \longrightarrow R_2Si: + R_2SiH_2 \qquad (12)$$
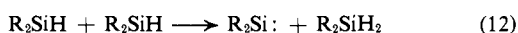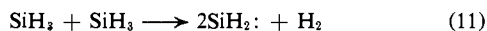
The data on the SiD$_4$ system (cf. Table I) appear to require step 11 in the mechanism, while step 12 in the mono- and dimethylsilane systems, although of minor importance relative to step 5, cannot be excluded.

The energy-transfer process in the silane–Hg* systems merits attention here since no quenching cross-section data have been previously reported for these molecules. Hg 6(^{3}P$_1$) atoms have been shown to be distinct electrophiles in their collisional electronic-relaxation processes.[12] Consequently, silanes would be expected to be more efficient quenchers for this species than paraffins, because the former are more nucleophilic in character. This follows from the fact that (a) the electronegativity of the Si atom (1.9) is lower than that of C (2.5) or H (2.1). Hence in the Si–H bond the H atom carries a partial negative charge and is hydridic rather than protonic as in the C–H bond. (b) The 3p–s σ-bond is weaker, greater in physical size, and more polarizable than the 2p–s σ-bond. This higher reactivity of the Si–H bond was indeed borne out by some recent quenching cross-section (σ_Q^2) measurements made on silanes in this laboratory.[13] Table IV lists some cross-section values for silanes in comparison with the corresponding paraffin molecules. Furthermore, from the data in Table V it would appear

that a similar trend exists for the specific quenching efficiency of the Si–H bonds as was established earlier for C–H bonds, i.e., H$_3$Si–H < MeH$_2$Si–H < Me$_2$HSi–H < Me$_3$Si–H. The strong suppressing effect of fluorine substitution on σ_Q^2 should also be noted.

Table IV. Quenching Cross-Section Values of Silanes and Paraffins for Hg 6(^{3}P$_1$) Atoms[a]

Si compound	σ_Q^2/A^2	C analog	σ_Q^2/A^2
SiH$_4$	26	CH$_4$	0.06
CH$_3$SiH$_3$	32	C$_2$H$_6$	0.10
(CH$_3$)$_2$SiH$_2$	33	C$_3$H$_8$	1.5
(CH$_3$)$_3$SiH	30	(CH$_3$)$_3$CH	6.8
(CH$_3$)$_4$Si	5.0	(CH$_3$)$_4$C	1.4
(CH$_3$)$_3$SiF	1.0		
(CH$_3$)$_2$SiF$_2$	0.19		

[a] See ref. 13.

Table V. Quenching Cross-Section Values per Bond

Compound	σ^2/A^2
Per Si–H Bond	
H$_3$Si–H	6.5
CH$_3$H$_2$Si–H	10.7
(CH$_3$)$_2$HSi–H	16
(CH$_3$)$_3$Si–H	30
Per C–H Bond	
(CH$_3$)$_3$SiH$_2$C–H	0.4
(CH$_3$)$_2$FSiH$_2$C–H	0.1
(CH$_3$)F$_2$SiH$_2$C–H	0.03
H$_3$C–H	<0.02
CH$_3$H$_2$C–H	~0.02
(CH$_3$)$_2$HC–H	~0.4
(CH$_3$)$_3$C–H	~3.4

(11) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963; F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962; E. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.
(12) Y. Rousseau, O. P. Strausz, and H. E. Gunning, J. Chem. Phys., 39, 962 (1962).
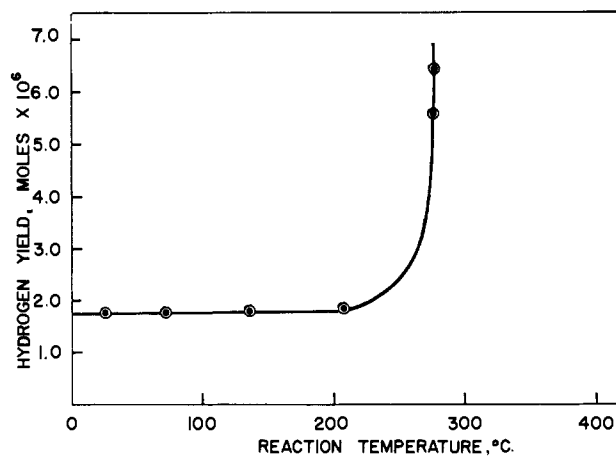(13) A. J. Yarwood, O. P. Strausz, and H. E. Gunning, ibid., 41, 1705 (1964).

The abstraction reaction 4 must occur at the same site in the molecule as the primary step 3, since only one kind of disilane is formed in each system with the exception of Me$_3$SiH, where small quantities of an isomeric disilane were also detected. If the pressures at which the maximum Φ(H$_2$) is achieved (cf. Figures 1, 3, 7, and 8 and Table VI) are an indication of the efficiency

of reaction 4, it follows that eq. 3 and 4 have parallel efficiencies in each silane system.

Table VI. Summary of Data for the Reactions of Substituted Silanes with Hg $6(^3P_1)$ Atoms

| Substrate | $\Phi(H_2)$ | Moles/einstein | | Δ^a | Approx. pressure at which $\Phi(H_2)_{max}$ is reached, mm. |
		$\Phi(H_2)_\infty$	Φ (disilane)		
MeSiH₃	0.80	0.81	0.72	0.08	200
Me₂SiH₂	0.81	0.81	0.71	0.10	200
Me₃SiH	0.80	0.81	0.78	0.02	250
Me₄Si	0.84	0.88	0.84	0.00	700
Me₂SiF₂	0.45ᵇ	1.0	0.44ᵇ	0.01	>1800
MeSiD₃	0.71	0.71	0.68	0.03	200

^{a} $\Delta = \Phi(H_2) - \Phi$(disilane). ^{b} Maximum values not reached.

The results of the time studies (Figures 2, 4, and 9) and the relative trisilane yield studies (Figures 5 and 6) suggest that the trisilane products are formed mainly if not entirely in secondary reactions. In the case of Me₄Si, Me₃SiH, and Me₂SiF₂, where Δ, the difference $\Phi(H_2) - \Phi$(disilane) taken at zero reaction time, is virtually zero as shown in Table VI, the destruction of the primary disilane product is due to attack by Hg*, H, or R (primary radical). The dimers from Me₄Si and Me₂SiF₂, which contain the reactive $-CH_2-CH_2-$ linkage, have considerably higher σ_Q^2 values than the substrate and, in addition, as a result of attack by the above species are capable of olefin formation; consequently, the time effect here (Figure 2) will be more pronounced than with Me₃SiH (Figure 4). The situation is somewhat different with Me₂SiH₂ and MeSiH₃. Here, Δ has a value of *ca.* 0.1 at zero exposure time (Table VI) and changes very little with time. On the other hand, Δ seems to be pressure dependent and at sufficiently high pressures may vanish. This behavior may be due to reactions such as (7) or (12), or alternately to the formation of vibrationally excited radicals in the primary step 3 which may subsequently undergo unimolecular hydrogen loss or collisional stabilization.

$$R* \begin{cases} \longrightarrow R' + H & (13a) \\ \\ \xrightarrow{M} R & (13b) \end{cases}$$
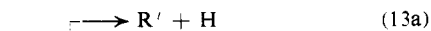
If the sum of the first and second Si–H bond dissociation energies in mono- and dimethylsilane was not much more than 112 kcal./mole, the excitation energy of Hg $6(^3P_1)$ atoms, then step 13a would be energetically possible. At present, however, there is no way to decide among these possibilities.

The study of the CH₃SiD₃ molecule was intended to yield information on the H–D isotope effect in the reaction. The paraffins have been shown to exhibit a large primary kinetic isotope effect.[14] Thus, on deuteration of the reactive methylenic hydrogens in propane, the primary *n*-propyl/isopropyl radical ratio changed markedly. As is evident from the data, no similar effect appears in the present case.

When reciprocal $\Phi(H_2)$ values are plotted against the

reciprocal of pressure (Figure 11), linear relations result for all of the six substituted silanes studied, thus satisfying the empirical equation

$$\Phi(H_2)^{-1} = \Phi(H_2)_\infty^{-1} + kp^{-1} \qquad (a)$$

Equation a has been previously applied for paraffin reactions.[15] The existence of such a relation can probably be explained by the asymptotic nature of the competition of step 3 with the fluorescence process
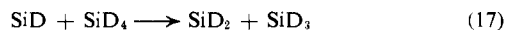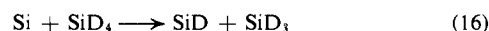
$$Hg* \longrightarrow Hg + h\nu \qquad (14)$$
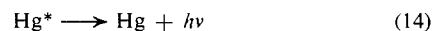
and of the competition of step 4 with 6. It is also likely that Lorentz-broadening of the absorption resonance line is a contributing factor.[16] In any case, the $\Phi(H_2)$ values change very little on extrapolation, when the quenching cross section of the substrate is large, but the change is quite appreciable when σ_Q^2 is small as for Me₂SiF₂. The extrapolated $\Phi(H_2)$ values are listed in Table VI along with a summary of the pertinent data obtained for the substituted silanes. As can be seen, even the extrapolated $\Phi(H_2)$ values are less than unity with the exception of Me₂SiF₂. No explanation for this inefficiency in the primary step can be offered at this time.

The decomposition of SiD₄ is complex and does not follow the general pattern found for the methylsilanes (CH₄ also behaves differently from the higher paraffins[17]). The great dependence of $\Phi(D_2)$ on the condition of the cell surface must be due to the wall-catalyzed decomposition of at least some of the primary reaction fragments. A knowledge of the homogeneous gas phase $\Phi(D_2)$ is essential in establishing the primary step of the reaction. From the incomplete study on this molecule, it is not possible to state the primary $\Phi(D_2)$ with certainty. Nevertheless, it appears that with increasing polymer coating on the walls, $\Phi(D_2)$ reaches a limiting value of *ca.* 3 (*cf.* Table I). With this provision the present data are compatible with the primary steps postulated by Niki and Mains.[3]

$$SiD_4 + Hg* \longrightarrow SiD_2 + 2D + Hg \qquad (15a)$$
$$\longrightarrow Si + 2D_2 + Hg \qquad (15b)$$
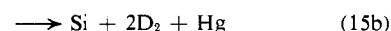
The bond dissociation energy of SiH₄ from the most recent electron-impact study was found to be 94 kcal.,[18] thus step 15a would be energetically possible if the second bond-dissociation energy is <18 kcal./mole, a value which is not impossible. These steps still could only provide a maximum $\Phi(D_2)$ value of 2, when followed by D-atom abstractions. The only conceivable additional D₂-producing reaction appears to be the disproportionation reactions of silyl radicals (step 11) which would be exothermic by more than 66 kcal./mole. Additional steps of possible importance are

$$Si + SiD_4 \longrightarrow SiD + SiD_3 \qquad (16)$$
$$SiD + SiD_4 \longrightarrow SiD_2 + SiD_3 \qquad (17)$$
$$D + SiD_4 \longrightarrow D_2 + SiD_3 \qquad (18)$$

(14) H. E. Gunning and O. P. Strausz, "Advances in Photochemistry," W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter IX, p. 209.
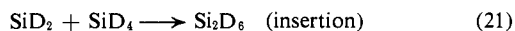
(15) B. de B. Darwent and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 381 (1948).

(16) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," The Macmillan Co., New York, N. Y., 1934.

(17) R. A. Back and D. van der Auwera, *Can. J. Chem.*, **40**, 2339 (1962).

(18) W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 4441 (1962); see also W. C. Steele and F. G. A. Stone, *ibid.*, **84**, 3599 (1962); G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, **86**, 3174 (1964).

$$2SiD_4 \longrightarrow Si_2D_6 \qquad (19)$$

$$nSiD_2 \longrightarrow (SiD_2)_n \qquad (20)$$

$$SiD_2 + SiD_4 \longrightarrow Si_2D_6 \quad \text{(insertion)} \qquad (21)$$

If the sum of the first and second bond-dissociation energies in silane is <112.7 kcal., the sum of the third and fourth ones must be $311 -$ max. $112.7 \geqslant 198.3$ kcal. and therefore either or both of steps 16 and 17 will be energetically possible. Reaction 21 would be of significance only if SiD_2 is in a singlet state. Skell and Goldstein[10] postulate a singlet electronic ground state for Me_2Si:

The ratio of primary steps 15a to 15b was estimated, from the run performed in the presence of ethylene (*cf.* Table I), to be within the range of 0.5 to 1.0. This estimate is based on the assumption that D atoms are completely scavenged by ethylene. The validity of this assumption, however, is subject to question in view of the postulated high efficiency of step 18.[3,19] Clearly more experimental work is needed to clarify this point. The high yield of D_2 in the presence of ethylene cannot be explained by the surface-catalyzed chain decomposition and therefore must be due to the high quantum efficiency of primary steps 15a and 15b.

The temperature study of the trimethylsilane reaction (*cf.* Table III) indicates a greater thermal stability for the Me_3Si radical than that for the Me_3C radical. Thus from the mercury $6(^3P_1)$ photosensitization of isobutane, an activation energy of <21 kcal./mole was established[20] for the decomposition reactions of *t*-butyl radicals. Now in comparing the activation energies for decomposition (E_D) for Me_3C and Me_3Si, it should be noted that in the former, E_D is lowered by the isomerization of Me_2C: to C_3H_6. In the analogous reaction for Me_3Si

$$Me_3Si\cdot \longrightarrow Me_2Si: + Me \qquad (22)$$
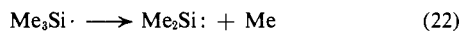
olefin formation is not possible, which probably accounts for the higher E_D for Me_3Si, compared to that for Me_3C.

Dimethylsilyl radicals appear to be stable up to $200°$. The rapid, ostensibly heterogeneous pyrolysis of the Me_2SiH_2 substrate, however, prevented study at higher temperatures.

It should be noted again that the mercury sensitization of neither Me_3SiH nor Me_2SiH_2 has a temperature coefficient, yet both have quantum yields less than unity (Table VI).

Finally, for the reactions of the NO–silane systems it is important to account for the products, H_2, N_2, and the disiloxane, as well as for the chain character of the reaction. In view of the incomplete product analysis and the inadequate kinetic data, only a very tentative mechanism can be suggested. Taking $MeR_2Si\cdot$, where R = H or Me, to represent the silyl radical formed in step 3 with the substrates $MeSiH_3$, Me_2SiH_2, and Me_3SiH,

(19) Niki and Mains[3] have estimated an activation energy for the abstraction reaction 18 of *ca.* 0.5 kcal. which was probably based on the lower Si–H bond energy value. Using the method of H. S. Johnston and C. Parr (*J. Am. Chem. Soc.*, **85**, 2544 (1963)), we computed E_a = 8.3 kcal. taking D(Si–H) = 94 kcal.[18] (which might be 2–3 kcal. too high).

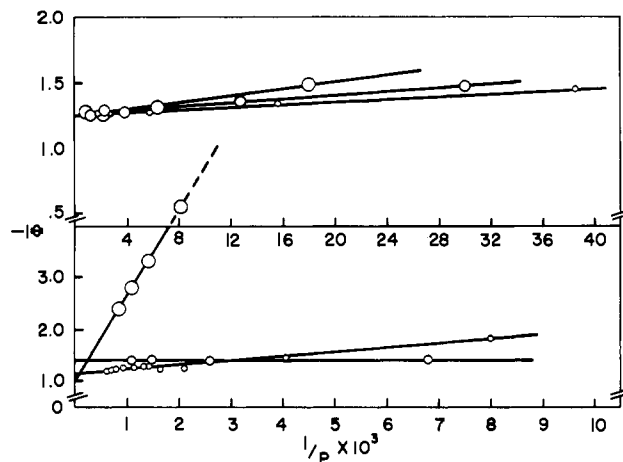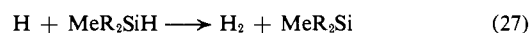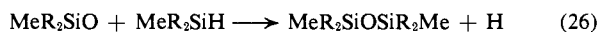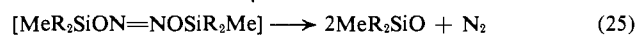(20) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 172 (1951).

Figure 11. Plot of reciprocal of $\Phi(H_2)$ *vs.* reciprocal of substrate pressure. Upper diagram: $MeSiH_3$ reaction (large circles); Me_3SiH reaction (medium circles); Me_2SiH_2 reaction (small circles). Lower diagram: Me_2SiF_2 reaction (large circles); $MeSiD_3$ reaction (medium circles); Me_4Si reaction (small circles).

we propose the sequence

$$MeR_2Si + NO \longrightarrow MeR_2Si\dot{O}N \qquad (23)$$

$$2MeR_2Si\dot{O}N \longrightarrow [MeR_2SiON=NOSiR_2Me] \qquad (24)$$

$$[MeR_2SiON=NOSiR_2Me] \longrightarrow 2MeR_2SiO + N_2 \qquad (25)$$

$$MeR_2SiO + MeR_2SiH \longrightarrow MeR_2SiOSiR_2Me + H \qquad (26)$$

$$H + MeR_2SiH \longrightarrow H_2 + MeR_2Si \qquad (27)$$

The "inverse" addition of NO to the silyl radicals, step 23 may be favored by the much higher affinity of silicon atoms for oxygen over nitrogen.[11] The resulting N–O-silyl biradical may be stabilized by the interaction of the unpaired electrons of the nitrogen with the unfilled d-orbitals of the silicon atom. Through an unstable dimer, the biradical is postulated to decompose to two siloxyl free radicals and N_2, *via* steps 24 and 25. Some support for the dimer formation comes from the fact that in the siloxane product fraction of the $MeSiH_3$ reaction, a compound with molecular weight of 240 was found in quantities of *ca.* 20% which structurally could be

$$\begin{array}{cc} MeSiH_2 & MeSiH_2 \\ | & | \\ MeH_2SiON\text{——————}NOSiH_2Me \end{array}$$
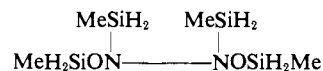
In the reactions of the resulting siloxyl radicals with silanes, the addition—again owing to the high silicon affinity towards oxygen—may occur on the silicon atom through the expansion of its valence shells, by the utilization of the vacant d-orbitals. The resulting adduct may stabilize itself by the loss of hydrogen, as shown in step 26, followed by abstractive regeneration of the silyl radical in step 27.

Further studies on the photochemistry of silicon compounds are in progress.