The Photochemistry of Silicon Compounds. III. The Vacuum-Ultraviolet Photolysis of Methylsilane

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Abstract: The gas-phase photolysis of methylsilane at the xenon and krypton resonance lines proceeds *via* the following primary steps with values of ϕ(Xe) and ϕ(Kr) given, respectively, in parentheses: $CH_3SiH_3 + h\nu \rightarrow$ (step 1) $CH_3SiH^* + H_2$ (0.32, 0.16); (step 2) $CH_3SiH + 2H$ (0.05, 0.09); (step 3) $CH_2SiH_2^* + H_2$ (0.23, <0.37 (0.14)); (step 4) $CHSiH_3 + H_2$ (0.07, 0.11); (step 5) $CH_4^* + SiH_2$ (0.09, 0.08); (step 6) $CH_3 + H + SiH_2$ (0.26, 0.25); (step 7) $CH_3 + H_2 + H + Si$ (0.00, 0.17); (step 8) $CH_3 + SiH_3^*$ ($\sim$0.02, 0.00). The total values of ϕ(Xe) and ϕ(Kr) are 1.04 and <1.23 (1.00), respectively. The asterisks signify hot products which may undergo further decomposition, thereby contributing to an additional apparent primary step. Increasing photonic energy increases this fragmentation. Final products in decreasing order of importance are H_2, $CH_3SiH_2SiH_2CH_3$, $CH_3SiH_2SiH_3$, CH_4, C_2H_6, $CH_3SiH_2CH_3$, SiH_4, and a solid polymeric material. The mechanism was deduced from the effect of exposure time, pressure, use of scavengers such as NO and C_2D_4, and deuterium labeling on product yields. The nature of products, in accord with the observed kinetics, unambiguously points to the intervention of two kinds of silene diradicals in the mechanism. They both are present in a singlet electronic state and readily insert into the Si–H bond of the substrate to give hot, methylated disilanes.

The photochemical behavior of silicon hydrides is little understood, and with the exception of a preliminary account of the present work,[1] no relevant data can be found in the literature. The triplet mercury-photosensitized decompositions of several silicon hydrides have been studied[2-5] and the methylated varieties manifested a similar behavior to paraffins. Monosilane, SiH_4, exhibits a more complex pattern of decomposition involving elimination of one, two, or more hydrogen atoms as well as molecular hydrogen, and further contributing to the complexity, a heterogeneous chain decomposition of one of the intermediates, probably the SiH_3 radical, occurs.

These studies have also yielded pertinent information on the chemical nature of methyl-substituted monovalent silyl radicals. Thus, trimethylsilyl radicals recombine quantitatively, but the lower methylated ones, containing at least one Si–H bond, could to a minor extent disproportionate to yield silene diradicals and the silane molecule. It has also been shown that silyl radicals can effectively be scavenged by relatively small concentrations of nitric oxide. This reaction affords disiloxane as a principal product in a chain reaction with the complete suppression of the recombination products.

The present study was undertaken to gain further insight into the photochemical behavior of silicon hydrides. Preliminary investigations[1] have shown that the analogy with the behavior of paraffins extends to the vacuum uv direct photolysis as well, as the predominant modes of decomposition are the molecular elimination reactions giving rise to the formation of the vaguely investigated family of silicon diradicals, the silenes, which are the silicon analogs of carbenes.

Experimental Section

Standard high-vacuum techniques were employed. All apparatus was stopcock grease-free, being equipped either with mercury float valves or Hoke TY440 valves. Two cylindrical reaction cells, 30 mm in diameter and 200 mm in length, fitted with LiF windows at the end, were used. The LiF windows were sealed to the reaction cells with black wax, and they were polished after each run to remove the polymer formed on the surface.

The xenon and krypton resonance lamps were air-cooled electrodeless discharges operated by a 2450-Mc/sec microwave generator. The xenon resonance lamp, emitting radiation[6] at 1470 Å (and 1295 Å whose intensity is *ca.* 2% of that of 1470 Å), and the krypton resonance lamp, emitting radiation at 1236 Å (and 1165 Å with intensity of *ca.* 28% of that of 1236 Å), were filled with 0.1 torr of Xe and of Kr, respectively, and about 1 torr of Ne as carrier gas. All gases used for lamps were obtained from Air Reduction Co. Barium getters (Kemet Co.) were used to eliminate residual gases.

The window of the lamp was placed in contact with the entrance window of the reaction cell and surrounded with a column of flowing nitrogen gas in order to remove oxygen which absorbs strongly the emission lines. Light intensities of Xe and Kr lamps, based on CO_2 actinometry (ϕ(CO) = 1.0),[7] were *ca.* 6×10^{15} and *ca.* 3×10^{15} quanta/sec, respectively. Because of attenuation of the incident light intensity during an experiment by polymer deposition on the cell face window, quantum yield values were determined from exposure time studies by extrapolation to zero exposure time.

CH_3SiH_3 (Peninsular) and CH_3SiD_3 (Merck) were purified prior to each run by low-temperature distillation at −130° and degassed at −160°. The extent of deuteration of CH_3SiD_3 on the silicon atom was determined to be 96.5% (D/(D + H)) by mass spectrometry. Ethylene-d_4 (Merck) was used without further purification. Nitric oxide (Matheson) was distilled at −183° and degassed at −196°.

In the series of quantitative measurements, the fraction noncondensable at −196° was removed by a Toepler pump and analyzed by a gas chromatograph on a molecular sieves column with Ar as carrier.

The condensable fraction was subsequently analyzed on a 16-ft 20% D.C. Silicon Oil 710 on Kromat C.E., using the Perkin-Elmer 881 flame-ionization gas chromatograph. Isotopic analyses of hydrogen and identification of products were performed by mass spectrometry.

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[1] O. P. Strausz, K. Obi, and W. K. Duholke, *J. Am. Chem. Soc.*, **90**, 1359 (1968).

[2] H. J. Emeleus and K. Stewart, *Trans. Faraday Soc.*, **32** 1577 (1936).

[3] D. White and E. G. Rochow, *J. Am. Chem. Soc.*, 76, 3987 (1954).

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[5] M. S. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965); also unpublished results from this laboratory.

[6] J. R. McNesby and H. Okabe, *Advan. Photochem.*, **3**, 157 (1964).

[7] B. H. Mahan, *J. Chem. Phys.*, **33**, 959 (1960).

Table I. Relative Product Yields as a Function of Exposure Time in the Photolysis of CH_3SiH_3 with a Xe Lamp[a] and Kr Lamp[b]

Time, min	Relative yield, %											
	H_2		CH_4		C_2H_6		DMS		MDS		DMDS	
	Xe	Kr	Xe	Kr	Xe	Kr	Xe	Kr	Xe	Kr	Xe	Kr
1	47.9	57.6	7.7	4.9	2.7	5.5	3.5	4.2	17.1	13.4	21.0	14.3
2	47.6	59.8	6.8	5.0	3.1	3.6	2.9	4.1	17.6	12.9	22.1	14.5
5	49.1	58.1	7.7	5.2	3.6	4.4	3.7	4.8	16.0	13.6	19.7	13.9
10	49.3	59.2	7.3	5.2	3.7	3.9	3.9	3.9	16.6	13.8	19.2	14.0
20	49.4	59.8	7.7	5.8	3.3	4.2	3.6	3.4	16.1	14.4	19.8	14.9

[a] $P(CH_3SiH_3)$ = 100 torr. [b] $P(CH_3SiH_3)$ = 100 torr.

Results

Products of the reaction of both wavelengths were of the same nature, but in somewhat different proportions. Beside hydrogen, which was the most abundant product, the following compounds, in decreasing order of importance, were also detected: 1,2-dimethyldisilane (DMDS), methyldisilane (MDS), methane, dimethylsilane (DMS), ethane, and monosilane. A solid polymeric material deposited on the walls was also formed, which caused a decrease in the transparency of the LiF window of the cell during an experiment. In order to overcome this difficulty in the quantum yield measurements and to distinguish between products of primary and secondary origin, an exposure time study was made at each wavelength. The results given in Table I indicate that product ratios are invariant with respect to exposure time; consequently they all are of primary origin.

A graphical extrapolation of the data to zero exposure time gave the following quantum yield values.

	H_2	CH_4	C_2H_6	DMS	MDS	DMDS
ϕ(Xe)	1.01	0.16	0.06	0.07	0.36	0.44
ϕ(Kr)	1.42	0.12	0.14	0.10	0.33	0.35

The higher absolute and relative yields of hydrogen as compared to the disilane yields at the higher energy photolysis reflect the increased importance of polyfragment decomposition[8] and/or secondary decomposition of initially hot products of the primary step to release additional hydrogen. The photonic energy available at 1470 Å is 195 kcal/einstein and at 1236 Å, 231 kcal/einstein. In addition a considerable fraction of the 1165-Å Kr resonance line with photonic energy of 245 kcal/einstein would also penetrate the cell. Though bond energies for silicon compounds are not well established, it may be estimated that the endothermicity of a polyfragment decomposition of $CH_3SiH_3 + h\nu \rightarrow CH_3 + H_2 + H + Si$ would not exceed 231 kcal/mole or $CH_3SiH_3 + h\nu \rightarrow CH_3 + H + SiH_2$, 195 kcal/mole. Therefore the occurrence of these and analogous processes to some extent may be anticipated.

Next, the effect of substrate pressure on product yields was examined in 20-min photolyses, and the results are plotted in Figures 1 and 2 for the xenon and krypton lamps, respectively. Three different trends can be observed. At both wavelengths the yields of CH_4, C_2H_6, and DMS are affected very little by pressure, while H_2 increases and DMDS and MDS decrease with decreasing pressure below 100 torr to some limiting values. Above 100 torr all product yields become nearly independent of pressure. The fact that the yield of the pressure-independent products remains invarient even at the lowest pressure, 3 torr, used indicates that the absorption of radiation is complete at this pressure already, manifesting the high extinction coefficient of methylsilane at these wavelengths. The similar behavior of the two disilanes suggests that they form by a similar mechanism, which is different from those of CH_4, C_2H_6, and DMS. Also the similar but opposite pressure dependence of the H_2 yield may be interpreted by the fragmentation of the disilane molecules with the release of hydrogen at low pressures. The remaining silicon fragment would presumably end up then in the solid polymer. To avoid complications due to the pressure-dependent fragmentations all subsequent experiments were conducted at a pressure of 100 torr or higher.

As mentioned above it has been shown in a previous study[5] on the mercury photosensitization of various methylated silanes that nitric oxide is an efficient scavenger of the monovalent silyl radicals. Therefore, if the principal products DMDS and MDS come from the combination reactions of monovalent radicals, their formation should be supressible by small concentrations of nitric oxide.

In order to sort out monoradical reactions from others, experiments were carried out in the presence of a few torr

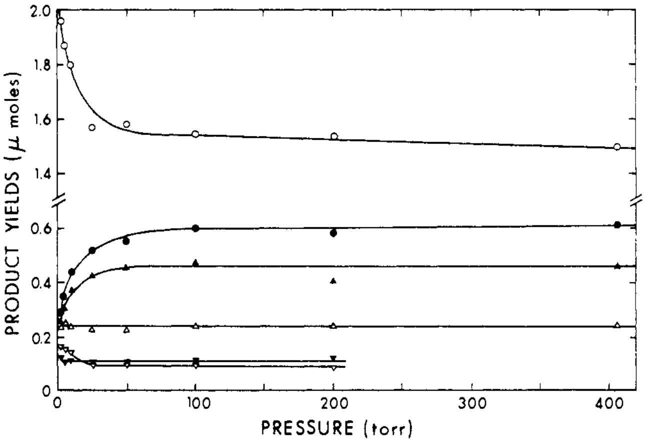

Figure 1. Product yields as a function of substrate pressure in the photolysis of CH_3SiH_3 with a Xe lamp, exposure time 20 min: ○, H_2; ●, $(CH_3SiH_2)_2$; △, CH_4; ▲, $CH_3Si_2H_5$; ▽, C_2H_6; ▼, $(CH_3)_2SiH_2$.

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[8] In the vacuum uv flash photolysis of methane, polyfragment decompositions, $CH + H_2 + H \leftarrow CH_4 + h\nu \rightarrow C + 2H_2$, have been proposed; *cf.* W. Braum, K. H. Welge, and J. R. NcNesby, *J. Chem. Phys.*, **45**, 2650 (1966); W. Braum, J. R. McNesby, and A. N. Bass, *ibid.*, **46**, 2071 (1967).

Table II. The Photolysis of CH_3SiH_3 in the Presence of NO[a]

CH_3SiH_3, torr	NO, torr	Lamp	Products, μmoles								
			H_2	N_2	CH_4	C_2H_6	DMS	MDS	DMDS	MDSO	DMDSO
99.8	0	Xe	1.03	0	0.12	0.08	0.12	0.34	0.42	0	0
100	1.28	Xe	2.20	0.71	0.37	0.00	Trace	0.34	0.31	0.10	0.29
97.9	1.98	Xe	2.31	1.20	0.48	...	0.00	0.50	0.48	0.12	0.49
100	0	Kr	0.77	0	0.07	0.06	0.06	0.18	0.22	0	0
102	1.27	Kr	0.97	0.42	0.09	0.00	Trace	0.11	0.14	0.03	0.26
100	2.51	Kr	1.06	0.67	0.14	0.00	Trace	0.14	0.14	0.03	0.33

[a] Exposure time 5 min.

Table III. Isotopic Composition of Hydrogen and Methane Formed in the Photolysis of CH_3SiH_3 + CH_3SiD_3 Mixtures with a Xe Lamp[a]

Total pressure, torr	CH_3SiH_3, %	Hydrogen, %			Methane, %	
		H_2	HD	D_2	CH_4	CH_3D
100.0	0	6.9	23.4	69.7	5.9	94.1
98.8	25.0	31.8	30.9	37.3	39.7	60.3
100.6	50.6	54.5	24.9	20.6	65.5	34.5
99.8	74.5	76.2	14.4	9.4	83.8	16.2
99.5	85.2	86.4	8.4	5.1	91.5	8.5

[a] Exposure time 20 min.

Table IV. Isotopic Composition of Hydrogen and Methane Formed in the Photolysis of CH_3SiH_3 + CH_3SiD_3 Mixtures with a Kr Lamp[a]

Total pressure, torr	CH_3SiH_3, %	Hydrogen, %			Methane, %	
		H_2	HD	D_2	CH_4	CH_3D
100.2	0	7.8	25.5	66.5	7.2	92.8
100.9	24.6	27.6	35.6	36.8	37.5	62.5
101.4	50.5	51.5	30.1	18.4	64.1	35.9
98.9	76.1	76.8	16.3	6.9	82.5	17.5
100.5	85.0	85.6	10.4	4.0	90.6	9.4

[a] Exposure time 20 min.

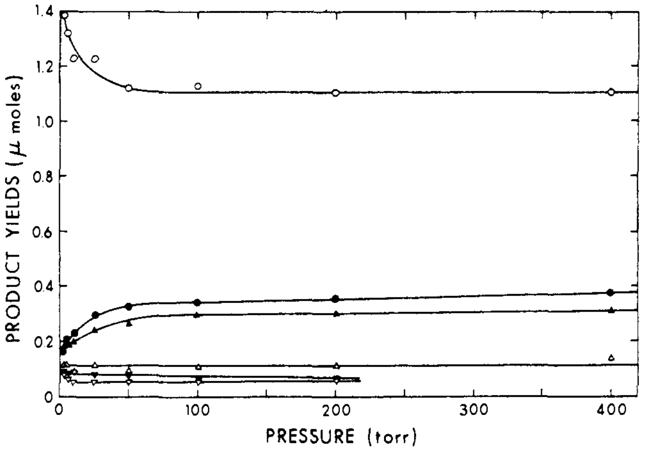

Figure 2. Product yields as a function of substrate pressure in the photolysis of CH_3SiH_3 with a Kr lamp, exposure time 20 min: ○, H_2; ●, $(CH_3SiH_2)_2$; △, CH_4; ▲, $CH_3Si_2H_5$; ▽, C_2H_6; ▼, $(CH_3)_2SiH_2$.

of added nitric oxide. Table II lists the results. Evidently C_2H_6 and DMS are wholly radical recombination products, but the two disilanes, their yield being affected but little by NO, in their majority form by some other mechanism.

The chain nature of the NO-inhibited reaction is apparent from the increasing yields of H_2, CH_4, and N_2 with increasing concentration of nitric oxide and also from the same trend in the yields of the new products methyldisiloxane (MDSO) and dimethyldisiloxane (DMDSO) which are indicative of the presence of the radicals SiH_3 and CH_3SiH_2 in the system.

The only remaining reasonable alternative to a monoradical precursor for the disilanes would be a silene-type intermediate which in an insertive attack on the substrate could give disilane. To examine this question deuterium-labeling techniques were applied.

Experiments were carried out with CH_3SiD_3 and various mixtures of CH_3SiD_3 and CH_3SiH_3. From a comparison of the photolysis of pure CH_3SiD_3 and CH_3SiH_3 no significant differences appeared in the overall rate of reaction at a pressure of 100 torr, and it was assumed that the extinction coefficients of the two molecules have approximately the same value. The isotopic composition of the hydrogen and methane products from this series of experiments is listed in Tables III and IV. The fractional yields of D_2 and HD after being corrected for absorption by CH_3SiD_3 are plotted as a function of CH_3SiH_3 concentration in Figures 3 and 4.

Before evaluating the results, some relevant information should be considered.

(a) Abstraction of a hydrogen atom by free radicals, including H atoms, is several orders of magnitude faster from Si–H than from the primary C–H bond.[9,10]

(b) A single C–H bond cleavage is only of minor importance in the photolyses of ethane,[6,11,12] propane,[6,13] and *n*-butane,[6] and a single Si–H bond cleavage should not be significant in the photolysis of methylsilane since the resulting fragment would carry even more excess energy than in the case of paraffins and further fragmentation should be just as facile. Besides, the nitric oxide scavenging experiments already have indicated that though CH_3SiH_2 radicals are present in the system they play a

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(9) J. A. Kerr, D. H. Slater, and J. C. Young, *J. Chem. Soc.*, *A*, 104 (1966); 134 (1967); T. N. Bell and B. B. Johnson, *Australian J. Chem.*, **20**, 1545 (1967).

(10) O. P. Strausz, E. Jakubowski, H. S. Sandhu, and H. E. Gunning, *J. Chem. Phys.*, in press.

(11) R. F. Hampson, Jr., and J. R. McNesby, *ibid.*, **42**, 2200 (1965); H. Akimoto, K. Obi, and I. Tanaka, *ibid.*, **42**, 3864 (1965).

(12) R. F. Hampson, Jr., J. R. McNesby, H. Akimoto, and I. Tanaka, *ibid.*, **40**, 1099 (1964).

(13) D. W. L. Griffiths and R. A. Back, *ibid.*, **46**, 3913 (1967).

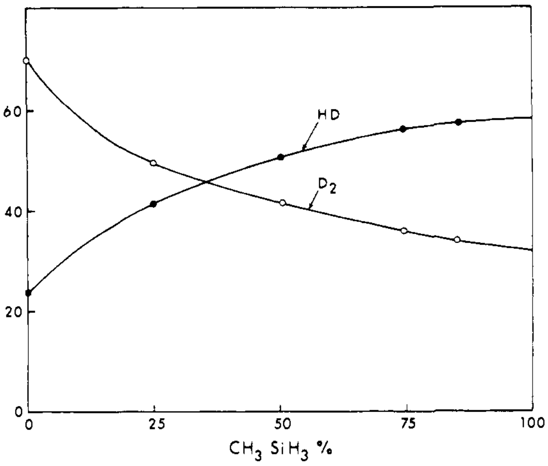

Figure 3. Fractional yield variation of D_2 and HD in the hydrogen product in the photolysis of CH_3SiH_3–CH_3SiD_3 mixtures with a Xe lamp, corrected for absorption by CH_3SiD_3 as a function of CH_3SiH_3 concentration.

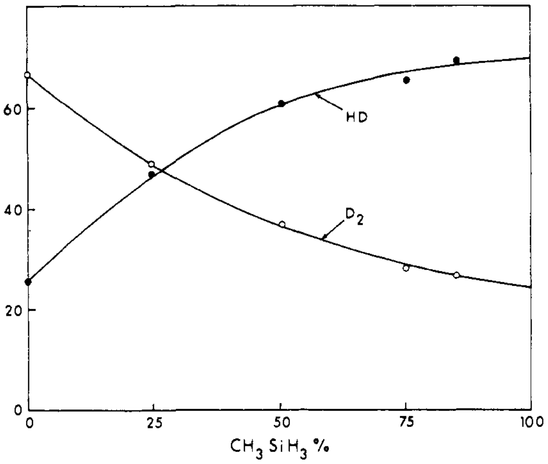

Figure 4. Fractional yield variation of D_2 and HD in the hydrogen product in the photolysis of CH_3SiH_3–CH_3SiD_3 mixtures with a Kr lamp, corrected for absorption by CH_3SiD_3 as a function of CH_3SiH_3 concentration.

relatively small role in the reaction.

Thus the H_2 product in the photolysis of pure CH_3SiD_3 must result from a molecular elimination of hydrogen in a primary step

$$CH_3SiD_3 + h\nu \rightarrow CHSiD_3 + H_2 \qquad (4)$$

The yield of H_2 at 1470 Å is 7% and the quantum yield of total hydrogen formation is 1.01; therefore $\phi(4) = 0.07$. The corresponding figures for the 1236-Å photolysis are 8% and 1.42, and $\phi(4) = 0.11$.

From this point it will be more appropriate to discuss the results of the Xe and Kr photolyses separately beginning with the former.

1470-Å Photolysis. The unscavengeable yield of D_2 as obtained from extrapolation to 100% CH_3SiH_3 concentration, Figure 3, is 32% and should be the measure of the extent of the molecular D_2-forming primary step

$$CH_3SiD_3 + h\nu \rightarrow CH_3SiD + D_2 \qquad (1)$$

with $\phi = 0.32$.

To explain the rising trend of the HD yield with increasing CH_3SiH_3 concentrations, we consider the following alternatives.

$$\begin{aligned} CH_3SiD_3 + h\nu &\rightarrow CH_3SiD + 2D && (2)\\ &\rightarrow CH_2SiD_2 + HD && (3)\\ &\rightarrow CH_2SiD_2 + H + D && (9)\\ &\rightarrow CH_3 + D + SiD_2 && (6) \end{aligned}$$

That step 9 is not operative was shown by scavenging experiments using C_2D_4, the results of which will be described later. Therefore HD in pure CH_3SiD_3 forms by primary step 3 with a quantum yield of 0.23. The increase in HD yield with increasing concentration of CH_3SiH_3 is then due to primary steps 2 and 6 with a combined quantum efficiency of 0.35 for D atom formation. To prove the occurrence of primary step 6 and to evaluate the efficiencies of eq 3 and 6 individually, we turn now to the methane-forming reaction.

From Table III it is seen that 94% of the methane formed in the photolysis of pure CH_3SiD_3 is CH_3D. The remaining 6% CH_4 largely comes from the isotopic impurity of the starting material. When the yield of CH_3D, after correction for fractional absorption by CH_3SiD_3, is plotted against the concentration of CH_3SiH_3, the curve given in Figure 5 is obtained. Extrapolation to 100% CH_3SiH_3 concentration gives a value of 56% for the yield of CH_3D that is unscavengeable. The measured quantum yield of methane formation is 0.16 and thus the quantum yield of molecular methane formation

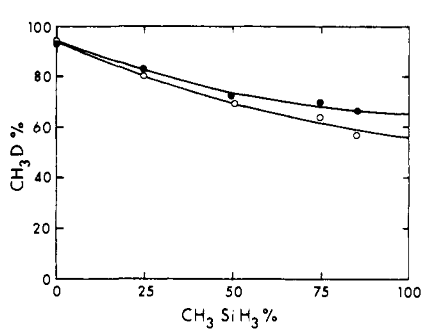

Figure 5. Fractional yield variation of CH_3D in the methane product in the photolysis of CH_3SiH_3–CH_3SiD_3 mixtures, corrected for absorption by CH_3SiD_3 as a function of CH_3SiH_3 concentration: ○, Xe lamp; ●, Kr lamp.

$$CH_3SiD_3 + h\nu \rightarrow CH_3D + SiD_2 \qquad (5)$$

is 0.09. The rest of the methane is formed by the abstraction reaction of methyl radicals.

$$CH_3 + CH_3SiD_3 \rightarrow CH_3D + CH_3SiD_2 \qquad (10)$$

The ethane and dimethylsilane products arise from the recombination reaction of methyl and the combination reaction of methyl with methylsilyl

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (11)$$

$$CH_3 + CH_3SiD_2 \rightarrow CH_3SiD_2CH_3 \qquad (12)$$

Thus the total quantum yield of methyl formation is $\phi(CH_4) - \phi(5) + 2\phi(C_2H_6) + \phi(DMS) = 0.26$. The two plausible methyl-forming primary steps to be considered are

$$\begin{aligned} CH_3SiD_3 + h\nu &\rightarrow CH_3 + SiD_3 && (8)\\ &\rightarrow CH_3 + D + SiD_2 && (6) \end{aligned}$$

Table V. Summary of Primary Quantum Yield Data for the Xe and Kr Lamp Photolyses

	ϕ(Xe)	ϕ(Kr)
$CH_3SiD_3 + h\nu \xrightarrow{1} CH_3SiD + D_2$	0.32	0.16
$\xrightarrow{2} CH_3SiD + 2D$	0.05	0.09
$\xrightarrow{3} CH_2SiD_2 + HD$	0.23	<0.37 (0.14)
$\xrightarrow{4} CHSiD_3 + H_2$	0.07	0.11
$\xrightarrow{5} CH_3D + SiD_2$	0.09	0.08
$\xrightarrow{6} CH_3 + D + SiD_2$	0.26	0.25
$\xrightarrow{7} CH_3 + D + D_2 + Si$	0.00	0.17
$\xrightarrow{8} CH_3 + SiD_3$	~0.01	0.00
Total	1.03	1.23 (1.00)

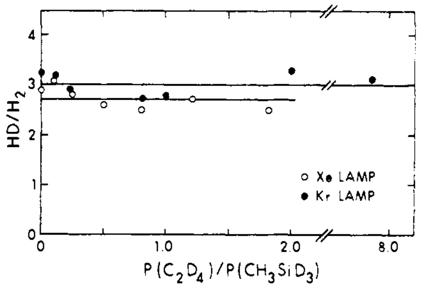

Figure 6. The HD/H_2 ratios in the photolysis of CH_3SiD_3–C_2D_4 mixtures as a function of $P(C_2D_4)/P(CH_3SiD_3)$.

Since the quantum yield for MDS formation is 0.36 and this product is not a radical combination product, step 6 appears to be the predominant methyl-forming primary step. The MDS is formed then from the insertion reaction of SiD_2 into the substrate.

$$SiD_2 + CH_3SiD_3 \rightarrow CH_3SiD_2SiD_3 \qquad (13)$$

If this reaction is quantitative, then ϕ(MDS) (=0.36) should be equal to $\phi(5) + \phi(6)$ (=0.09 + 0.26 = 0.35) which is the case within experimental error. The slightly higher yield of MDS (0.01) may be real and in conjunction with the appearance of trace quantities of SiH_4 among the products, and the appearance of small amounts of MDSO in the NO scavenging experiments would seem to point to the possibility of the contribution of a primary step

$$CH_3SiD_3 + h\nu \rightarrow CH_3 + SiD_3 \qquad (8)$$

to a minor extent of the over-all decomposition.

Reconsidering now the efficiency of the D-atom-producing primary steps, we stated above that $\phi(2) + \phi(6) = 0.35$ in terms of D-atom formation. Since $\phi(6) = 0.26$, it follows that $\phi(2) = 0.09$ in terms of atoms corresponding to $\phi(2) = 0.05$ in terms of primary step.

The primary quantum yield data for the xenon as well as the krypton line photolyses are summarized in Table V.

It now remains to be shown that primary step 9 is not operative to a significant extent. This was accomplished by scavenging experiments using C_2D_4. First the relative rates of the reactions

$$D + C_2D_4 \rightarrow C_2D_5 \qquad (14)$$

$$D + CH_3SiD_3 \rightarrow CH_3SiD_2 + D_2 \qquad (15)$$

were determined in an auxiliary study as $k(14)/k(15) = 5.5$. Next experiments were carried out (the results of which are depicted in Figure 6) on the photolysis of CH_3SiD_3 in the presence of varying amounts of C_2D_4, and the relative yields of HD to H_2 measured as a function of added C_2D_4. If primary step 9 is operative, the HD product should arise by the abstraction reactions of H atoms

$$H + CH_3SiD_3 \rightarrow HD + CH_3SiD_2 \qquad (16)$$

while H_2 from the molecular elimination reaction 4 and their ratio should diminish with increasing amounts of added ethylene. As seen from the figure the ratio is not affected by added ethylene, indicating that HD in pure CH_3SiD_3 forms in a molecular process.

As a further check on material balance we may consider the yield of DMDS in correlation with the quantum yield of the methylsilene producing primary steps 1 and 2. If DMDS arises from the insertion of methylsilene into the Si–H bond of the parent molecule

$$CH_3SiD + CH_3SiD_3 \rightarrow CH_3SiD_2SiD_2CH_3 \qquad (17)$$

then ϕ(DMDS) should be equal to $\phi(1) + \phi(2) = 0.37$. The experimental value of ϕ(DMDS) is, however, somewhat larger, 0.44.

If the silylmethylene from primary step 4 would also undergo a similar insertion reaction

$$CHSiD_3 + CH_3SiD_3 \rightarrow Si_2C_2H_4D_6 \qquad (18)$$

ϕ(DMDS) should be 0.44, in agreement with experiment. This, however, does not seem to be the case. Gc analysis gave only one peak corresponding to the retention time of DMDS, and the mass spectrometric analysis indicated an isotopic composition of $Si_2C_2H_6D_4$ with no significant amount of $Si_2C_2H_4D_6$. Thus it appears that the fraction of DMDS, 0.44 − 0.37 = 0.07, forms by the recombination of the monovalent methylsilyl radicals

$$CH_3SiD_2 + CH_3SiD_2 \rightarrow DMDS \qquad (19)$$

and the silylmethylene species undergo unimolecular isomerization

$$CHSiD_3 \rightarrow CHDSiD_2 \qquad (20)$$

rather than bimolecular insertion, and end up in the polymer fraction.

The total yield of CH_3SiD_2 radicals produced in the system can be obtained from the yield of D atoms and the amount of methyl radicals which underwent D-atom abstraction reaction with the substrate. Thus $\phi(CH_3SiD_2) = 2\phi(2) + \phi(6) + \phi(\text{methane}) - \phi(5) = 0.10 + 0.26 + 0.16 - 0.09 = 0.43$. From this, apparently 0.14 recombines to give DMDS, 0.07 combines with methyl to give DMS, and the remaining fraction 0.22 ends up in the polymer. The total yield of CH_2SiD_2 and $CHDSiD_2$ constituting the rest of the polymer is equal to $\phi(3) + \phi(4) = 0.30$. From this an average polymer molecule would consist of three diradicals and two monoradicals and have an empirical formula of $Si_5C_5H_{22}$.

1236-Å Photolysis. Similar experiments were conducted as in the 1470-Å photolysis. The data are presented in Tables IV and V and Figures 4–6. Owing to extensive fragmentation reactions, it is more difficult to unravel the primary decomposition mechanism here than in the Xe line photolysis.

Determination of the quantum yield of the molecular methane elimination reaction is relatively straightforward. ϕ(methane) is 0.12 of which 65% (Figure 5) is formed in a molecular process. Therefore $\phi(5) = 0.08$.

From the decrease of D_2 yield in Figure 4 on going from pure CH_3SiD_3 to pure CH_3SiH_3, $\phi(2) + \phi(6) = 0.61$ in terms of D atoms. Since $\phi(SiD_2) = \phi(MDS) = 0.33 = \phi(5) + \phi(6) = 0.08 + \phi(6)$, the yield of steps 6 and 2 are 0.25 and 0.18, respectively.

The quantum yield of methyl production can be obtained from $\phi(DMS) + 2\phi(C_2H_6) + \phi(CH_4) - \phi(5)$ and equals 0.42. When this is compared to $\phi(6) = 0.25$, it is seen that there is 0.17 more methyl formed than SiD_2. This requires another primary step, giving rise to CH_3 without the formation of silene. Several possibilities offer themselves. The most likely one will be the one which gives the highest yield of hydrogen within energetic restrictions and yields of methylsilene consistent with the yield of DMDS formation. Thus we prefer

$$CH_3SiD_3 + h\nu \rightarrow CH_3 + D + D_2 + Si \qquad (7)$$

to

$$CH_3SiD_3 + h\nu \rightarrow CH_3 + D_2 + SiD \qquad (21)$$

or

$$CH_3SiD_3 + h\nu \rightarrow CH_3 + 3D + Si \qquad (22)$$

Step 21 would give too high yields for CH_3SiD, and step 22 would be energetically unfavorable.

The quantum yield of (7) is given by the difference $\phi(CH_3) - \phi(SiD_2) = 0.17$. The D-atom yield from (7) should then be deducted from $\phi(2)$ calculated above. Thus the corrected quantum yield of (2) will be 0.09.

The data in Figure 4 indicate a ϕ value of 0.33 for molecular D_2 elimination. Since the contribution of primary step 7 is only 0.17, the remaining portion, 0.16, should come from primary step 1.

Molecular HD elimination is also operative with an apparent quantum yield of 0.37. This should partly come from primary step 3 and since the total quantum yield value for all primary steps considered would exceed unity, partly from secondary fragmentation of hot primary products. It would therefore appear that a large portion of the diradical CH_2SiD_2 formed in (3) undergoes further HD loss

$$\begin{tikzcd} CH_2SiD^*_2 \arrow[r] & CHSiD^* + HD \arrow[dl] \\ HD + CSi & \end{tikzcd} \qquad (23)$$

Energetically this process is favorable at the Kr line, but not at the Xe line.

A comparison of $\phi(CH_3SiD)$ with that of DMDS suggests that, as in the xenon line photolysis, a fraction of the DMDS forms from the recombination of methylsilyl radicals. This amount is quite similar in the two systems (0.1 and 0.14) reflecting the fact that though the quantum yield of CH_3SiD_2 production is higher in the Kr than Xe system the steady-state concentration of the radicals is about the same, owing to the lower intensity of the Kr lamp.

Discussion

From the data presented in the preceding section, a fairly comprehensive and self-consistent picture of the primary photochemical decomposition of silicon hydrides emerges. The over-all behavior bears a great deal of resemblance to that of the saturated carbon hydrides with some significant distinctions which arise from, and reflect on, the characteristic differences between the chemical nature of the carbon and silicon atoms.

Three distinct types of primary processes can be observed: one involving only silicon–hydrogen bond cleavage, one only carbon–hydrogen bond cleavage, and one which leads to carbon–silicon bond scission. The occurrence of several simultaneous and competing primary processes is probably related to spectral causes and to the fluctuations of internal energy in the excited state and random accumulation in one particular bond.

Very little is known about the spectra of silicon hydrides. Owing to the lower electronegativity of Si than C atoms, a red spectral shift can be expected as compared to paraffins. Indeed SiH_4 absorbs up to ~1800 Å, whereas the long-wavelength absorption onset of CH_4 is around 1430 Å. Disilane absorbs up to 2100 Å and can be readily photolyzed at this wavelength,[14] whereas ethane absorption occurs only below *ca.* 1600 Å.[15] The absorption spectrum of methylsilane extends up to about 1900 Å, and photolysis can be affected by the 1800–1900-Å line system of an iodine lamp.[16] The extinction coefficient in this region, however, is low. At 1236- and 1470-Å absorption in a 200-mm path-length absorption is complete at 3 torr cell pressure, whereas at 1800–1900 Å it is incomplete even at 800 torr and exhibits an H/D isotope effect; CH_3SiH_3 photolyzes at twice the rate of CH_3SiD_3 (at 400 torr). The ethane spectrum consists of a weak, forbidden transition at 1575 Å and much more intense allowed transitions at 1319 Å and shorter wavelengths. The 1319-Å band shows well-developed vibrational fine structure. These transitions may broadly be characterized as (σ,σ^*)-type transitions, the first one corresponding to the promotion of one of the (C–C) σ electrons to a 3s molecular orbital while the second one to the promotion of a (C–H) σ electron to the same excited orbital. Since the terminal orbitals in the two transitions are common, but in the former case the promoted electron comes from a bonding C–C orbital while in the latter case from a bonding C–H orbital, the first transition should give rise to relatively more C–C bond cleavage than the second. This prediction cannot be checked for lack of experimental data. All photolysis reactions of ethane have been carried out at 1470 Å and shorter wavelengths (the 1470-Å xenon line lies in the tail section of the first and head section of the second transition). Comparison of the 1470- and 1236-Å photolyses indicates that C–C bond rupture is more important at the shorter wavelength.[11] But whether this is due to an electronic effect or only to the higher excess of vibrational energy of the excited molecule is not clear. The second transition possesses clearly discernible vibrational fine structure which shows that the upper state is not repulsive or highly predissociative. From the moderately intense absorption the radiative lifetime may be roughly estimated to be ~10^{-7} sec. The fact that no emission has been observed from ethane (or paraffins in general) indicates that the dissociative lifetime should be at least three–

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(14) O. P. Strausz, H. Makada, and H. E. Gunning, submitted for publication.

(15) H. Okabe and D. A. Becker, *J. Chem. Phys.*, **39**, 2549 (1963).

(16) K. Obi, O. P. Strausz, and H. E. Gunning, submitted for publication.

four orders of magnitude shorter than the radiative one, that is, 10^{-10}–10^{-11} sec. Indeed, McNesby, *et al.*, have shown experimentally that the lifetime is shorter than 10^{-9} sec.[12] On the other hand, it cannot be considerably shorter than 10^{-11} sec since vibrational fine structure appears in the spectrum.

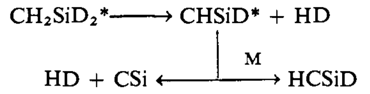
In lieu of spectral information on the methylsilane molecule, it may be permissible to assume a situation similar to that of ethane, except that the spectrum is shifted by about 300 Å to the red. Thus the 1470-Å Xe line would lie in the tail section of the second intense absorption and the 1236-Å krypton line perhaps in a higher energy transition region. At both wavelengths there may be more than one transition possible, giving rise to different electronic states. One may be tempted to presume that processes involving only Si–H bond cleavages (primary steps 1 and 2) arise from absorption by this bond, while decomposition involving only C–H cleavage (step 4) arises from absorption by this moiety. This assumption would then lead to values of ~0.2 and 0.4 for the ratio of the two competing absorptions at 1470 and 1236 Å, respectively. Against this militates the observation that in the 1800–1900-Å photolysis of CH_3SiD_3 the hydrogen fraction still contains about 9% H_2, although C–H bond absorption should diminish here. This result is significant in that it is a clear indication that absorption in one moiety of a saturated hydride molecule can lead to the rupture of other bonds of the molecule, although it is not surprising in view of the strongly delocalized nature of the excited orbital.

The data indicate that pressure up to 1 atm has no effect on the primary quantum yield values, and consequently the decomposition lifetime of the excited molecules should be in the order of 10^{-10} sec or shorter.

The hydrogen-producing primary steps 1, 3, and 4 are the counterpart of the hydrogen-producing decompositions of ethane. That molecular elimination of hydrogen from the silicon atom is more facile can be explained by the considerably lower strength of the Si–H than C–H bond. These bond-energy values are not known for the methylsilane molecule but inferred from general values,[17,18] $D(CH_3\text{–}H) = 104$, $D(SiH_3\text{–}H) = 95$, $D(CH_2\text{–}H) = 105$, $D(SiH_2\text{–}H) \sim 59$ kcal/mole (calculated);[17] therefore H_2 removal from the silicon end is approximately 60 kcal/mole less endothermic than from the carbon end. The resulting fragments CH_3SiH and H_2 carry about 145 kcal excess energy at the xenon lines and 180 kcal at the krypton lines. In the former case there is no evidence for the decomposition of the methylsilene fragment, and the main portion of the excess energy must be carried away by the H_2 molecule. In the latter case primary step 7 may be viewed as a special case of primary step 1 in which enough excess energy is left in the methylsilene fragment to bring about its fragmentation into $CH_3 + H + Si$. The energy requirement of this fragmentation should not exceed 160 kcal.

Primary step 3 in the case of ethane is accompanied by further H_2 loss from the resulting hot ethylene molecule to give acetylene. This process is pressure depedent[12] but cannot be completely suppressed by pressure even at 1470 Å. With methylsilane we find no evidence for further hydrogen release from the $\cdot CH_2SiH_2 \cdot$ diradical at 1470 Å, but extensive dehydrogenation occurs at 1236 Å. This diradical appears to be quite stable and is the precursor of the solid polymeric product of the reaction. The silicon atom does not form double bonds; therefore with methylsilane step 3 is energetically less favorable than with ethane, where the olefinic π-bond formation assists in the H_2 elimination. The endothermicities are roughly 40 kcal for C_2H_6 and 90 kcal for CH_3SiH_3, though weak interaction between the half-filled carbon and silicon p orbitals could somewhat decrease this latter figure. This could perhaps explain why the two H-atom releasing step is favored over the molecular H_2 elimination with ethane.

In the 1236-Å photolysis of CH_3SiD_3, the excessive amount of molecular HD formation from reaction 24 raises



$$\begin{tikzcd} \mathrm{CH_2SiD_2^*} \arrow[r] & \mathrm{CHSiD^* + HD} \arrow[d, dash] & \\ \mathrm{HD + CSi} & {} \arrow[l] \arrow[r, "M"] & \mathrm{HCSiD} \end{tikzcd} \qquad (24)$$

the over-all quantum yield of decomposition to 1.23. If we assume a value of unity for ϕ(primary), then ϕ(3) becomes 0.14. From this it appears that all $CH_2SiD_2^*$ decomposes to $HCSiD^*$ and 64% of the latter species to CSi (at a pressure of 100–400 torr).

Primary step 2 is a distinction from the behavior of ethane. The reason again probably lies in energetics. This step would require about 200 kcal with ethane and therefore would not be feasible at 1470 Å. With methylsilane the estimated energy requirement is about 150 kcal.

Comparing the four hydrogen-producing primary steps at the two wavelengths, it is seen that the more endothermic reactions always gain in importance with increasing photonic energy, and the effect is more pronounced the higher the endothermicity. This is illustrated by the data listed in Table VI.

Table VI. Correlation between Endothermicity and Relative Efficiency for the Four Hydrogen-Producing Primary Steps as a Function of Wavelength

Reaction	ΔH, kcal	ϕ/ϕ(1) 1470 Å	 1236 Å	ϕ/ϕ(1) at 1236 Å / ϕ/ϕ(1) at 1470 Å
(1) $CH_3SiH + H_2$	50	1.0	1.0	1.0
(3) $CH_2SiH_2 + H_2$	90	0.72	0.87	1.2
(4) $CHSiH_3 + H_2$	100	0.22	0.69	3.1
(2) $CH_3SiH + 2H$	150	0.16	0.56	3.5

The four primary steps, 5–8, leading to carbon–silicon bond cleavages have combined quantum yield values of ~0.36 at 1470 Å and 0.50 at 1236 Å. This trend also tallies with that established for ethane. It is to be noted here that the photolysis in the 1800–1900-Å lines, which possibly correspond to the first forbidden absorption band of ethane ((C–C)σ → 3s*), also leads to extensive C–Si bond cleavage,[16] which is consistent with the assumption that the transition here involves the promotion of a C–Si bonding electron.

In the C–Si bond-cleavage reactions the molecular mode

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of elimination of methane as compared to the radical mode of decomposition is relatively less important than in the ethane photolysis. The reason for this becomes evident by inspecting Table VII which lists the estimated enthalpy changes of primary steps 5–8 and the amounts of excess energy at the two wavelengths of the photolysis. The methane molecule formed in step 5 can possess excess energy up to 190 kcal, but in the ethane reaction the maximum excess energy is only 109 kcal. Thus in the methylsilane reaction a good portion of the methane can be expected to undergo hydrogen-atom loss giving rise to the apparent primary step 6. At the krypton line the excess energy becomes so large that not only the methane but the SiH_2 molecule could decompose as well, giving rise to the apparent primary step 7.

Table VII. Energetics of the C–Si Cleavage Primary Steps

Reaction	ΔH, kcal	Excess energy, kcal 1470 Å	 1236 Å
(5) $CH_4 + SiH_2$	41	144	190
(6) $CH_3 + H + SiH_2$	145	40	86
(7) $CH_3 + H_2 + H + Si$	201	−6	30
(8) $CH_3 + SiH_3$	86	109	145

An alternate mode of molecular decomposition would be

$$CH_3SiH_3 + h\nu \rightarrow CH_2 + SiH_4 \qquad (25)$$

which would be about 50 kcal less exothermic than (5) and appears to play an insignificant role. Nonetheless, as mentioned above, very small quantities of SiH_4 were detected among the reaction products, which could arise either by (25) or (8), or both.

At last it should be pointed out that the mechanism of the primary decomposition and the relative importance of the individual primary steps are somewhat dependent on the value of absolute quantum yield which in turn is based on the assumption that the CO yield of the CO_2 photolysis is unity. Problems associated with chemical actinometry in the vacuum uv region has been recently discussed by Ausloos and Lias.[19] The unit quantum efficiency of methylsilane decomposition at 1470 Å and the near unit efficiency at 1236 Å would seem to lend support to Mahan's value of $\phi(CO) = 1.0$ from CO_2 (under the conditions which prevailed in our experiments).

The two principal end products of the reaction, DMDS and MDS, largely arise by the insertion of the methylsilene and silene species into the Si–H bond of the parent molecule

$$CH_3SiH + CH_3SiH_3 \rightarrow CH_3SiH_2SiH_2CH_3 \qquad (17)$$

$$SiH_2 + CH_3SiH_3 \rightarrow CH_3SiH_2SiH_3 \qquad (13)$$

Theoretical calculations[17] predicts a singlet A_1 ground state for SiH_2 with a lowest excited $^1B_1$ state at ~60 kcal and a $^1A_1$ excited state at 73–84 kcal. A $^1A_1$ state has also been detected spectroscopically, but it could not be decided whether this is the ground state.[20]

The SiH_2 formed in step 6 in the 1470-Å photolysis may only be in the ground $^1A_1$ or excited $^1B_1$ state; otherwise either of the three states may be involved. Calculations are not available on the methylsilene species, but it is reasonable to assume that the methyl group would not significantly disturb the electronic situation. Thus again CH_3SiH formed in the less exothermic reaction 2 at 1470 Å is probably in the ground electronic state, while in the other reactions either of the excited singlet states may be involved. The fact that the two insertion products exhibit a gradual decline with decreasing pressure below 100 torr seems to favor the involvement of excited silene species in the reaction. From the somewhat unreliable bond-energy values involving the silicon atom, it may be estimated that the insertion reactions 13 and 17 would be exothermic to the extent of *ca.* 15 ± 5 kcal; this would be insufficient to bring about the fragmentation of the newly formed insertion products, since methyldisilanes are quite stable compounds. The involvement of electronically excited silenes would increase the exothermicity with an amount equivalent to the excitation energy and could explain the observed pressure effect. Naturally, vibrational excitation of the ground-state SiH_2 could produce the same result.

Similar insertion reactions for dimethylsilene,[21] trimethylsilene,[22] and silene itself[23] have been postulated before, based mainly on the nature of products derived from the reactions. In the present case this was further supplemented by detailed studies on deuterium labeling, quantum yield measurements, stoichiometry, and inhibition studies with ethylene and nitric oxide.

In the present as in the earlier studies the silene species were found to insert exclusively into the Si–H bond, and as mentioned above this reaction appears to be quantitative above 100 torr of CH_3SiH_3 pressure. A strong preference for Si–H over C–H insertion has also been observed with singlet methylene from the photolysis of ketene[24] and diazomethane[25] and with singlet-D sulfur atom[26] from the photolysis of COS. This increased reactivity of the Si–H bond in insertion reactions may be the consequence of the combined effects of its hydridic character, relatively low strength, and the availability of the vacant d orbitals of the silicon atom.

It remains to comment on the high stability of methylsilene with respect to unimolecular isomerization. The stability of this species at least in its ground electronic state is likely related to the peculiar trend in the Si–H bond dissociation energies for which Jordan[17] calculated the following values: $D(H_3Si\text{–}H) = 95$, $D(H_2Si\text{–}H) = 59$, $D(HSi\text{–}H) = 82$, $D(Si\text{–}H) = 74$ kcal/mole. In part I of this series[5] we also considered the possibility of a very large drop in $D(H_2Si\text{–}H)$ on experimental grounds. Our quantum yield measurement for the triplet mercury photosensitization of SiH_4 ($\phi(H_2) \sim 3$) and the observation that SiH_3 suffers an efficient breakdown to SiH_2 and H on quartz surfaces at room temperature led us to consider a

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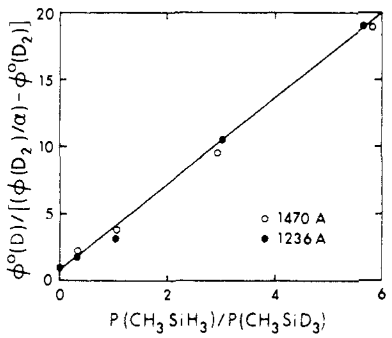

Figure 7. Plot in accordance with eq 28 of the data presented in Figures 3 and 4.

value of ⩽20 kcal for $D(H_2Si\text{-}H)$. In any case the isomerization reaction

$$CH_3SiH \rightarrow CH_2\text{—}SiH_2 \qquad (26)$$

would be unfavorable (*cf.* Table VI) and does not seem to occur at room temperature. This represents a significant departure from the behavior of the carbon counterpart ethylidene where the energies of bonds involved in the rearrangement are not too different and the formation of the olefinic π bond makes the reaction strongly exothermic. In contrast, we had to conclude on an experimental basis that the rearrangement

$$CH\text{—}SiH_3 \rightarrow CH_2\text{—}SiH_2 \qquad (20)$$

which should be about 10 kcal (plus the interaction energy of the C and Si half-filled orbitals) exothermic is quite rapid since silylmethylene could not be trapped.

Finally, the present data make it possible to estimate the H/D kinetic isotope effect of the hydrogen-abstraction reaction

$$D + CH_3SiH_3 \rightarrow CH_3SiH_2 + HD \qquad (27)$$

$$D + CH_3SiD_3 \rightarrow CH_3SiD_2 + D_2 \qquad (15)$$

Steady-state treatment gives

$$\frac{\phi^0(D)}{[(\phi(D_2)/\alpha) - \phi^0(D_2)]} = 1 + \frac{k_{27}}{k_{15}}\frac{[CH_3SiH_3]}{[CH_3SiD_3]} \qquad (28)$$

where $\phi^0(D)$ and $\phi^0(D_2)$ are the quantum yields of atomic D and molecular D_2 formation in pure CH_3SiD_3 photolysis, $\phi(D_2)$ is the measured quantum yield of D_2 formation from CH_3SiH_3-CH_3SiD_3 mixtures, and α is the mole per cent of CH_3SiD_3. Using the data presented in Figures 3 and 4, and plotting the left-hand side of the equation against $P(CH_3SiH_3)/P(CH_3SiD_3)$, a linear relation is obtained as shown in Figure 7. From the slope we obtain

$$k_{27}/k_{15} = 3.2$$

This appears to be a plausible value when compared to the H/D isotope effects recently measured in our laboratory for the reactions

$$CH_3 + SiH_4 \rightarrow CH_4 + SiH_3$$

$$CH_3 + SiD_4 \rightarrow CH_3D + SiD_3$$

and

$$CH_3 + Si_2H_6 \rightarrow CH_4 + Si_2H_5$$

$$CH_3 + Si_2D_6 \rightarrow CH_3D + Si_2D_5$$

as 5.0 and 5.5, respectively.[10]

Further studies are in progress.

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