Photochemistry of Silicon Compounds. IV. Mercury Photosensitization of Disilane

T. L. Pollock, H. S. Sandhu, A. Jodhan, and O. P. Strausz*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received June 23, 1972*

Abstract: The room-temperature mercury $6(^3P_1)$ photosensitization of disilane produces H_2, SiH_4, Si_3H_8, Si_4H_{10}, and a solid deposit. From detailed kinetic studies using deuterium-labeling techniques and scavengers such as NO and C_2H_4 it has been established that the sole primary step is $Hg\ 6(^3P_1) + Si_2H_6 \rightarrow Hg + H + Si_2H_5$, $\phi \approx 1.0$. Hydrogen atoms react with disilane *via* two steps: $H + Si_2H_6 \rightarrow SiH_4 + SiH_3$, $\phi = 0.34$, and $H + Si_2H_6 \rightarrow H_2 + Si_2H_5$, $\phi = 0.66$. The ensuing reactions of mono- and disilyl radicals have been investigated. The disilyl radical undergoes disproportionation and recombination reactions, $Si_2H_5 + Si_2H_5 \rightarrow Si_4H_{10}^{\ddagger}$, $Si_4H_{10}^{\ddagger} \rightarrow Si_2H_6 + SiH_2SiH_2$, and $Si_4H_{10}^{\ddagger} + M \rightarrow Si_4H_{10} + M$, which are pressure dependent up to several hundred Torr of Si_2H_6, but the monosilyl radicals only disproportionate up to atmospheric pressures. Unimolecular rate constants for the decomposition of chemically activated Si_2H_6 to SiH_2 and SiH_4 have been calculated using the RRKM theory. At elevated temperatures the disilyl radical attacks disilane *via* the displacement reaction $Si_2H_5 + Si_2H_6 \rightarrow Si_3H_8 + SiH_3$.

The triplet mercury photosensitization of methyl-, chloro-, and phenyl-substituted silanes as well as monosilane has been studied.[1-6] The methylsilanes undergo exclusive Si–H bond cleavage yielding hydrogen and the silyl dimer as final products.[1] In the case of chlorosilanes, the major process is also Si–H bond rupture resulting in hydrogen and chlorinated silanes.[2] Phenylsilane-d_3 suffers both C–Si and Si–D bond cleavage in the primary quenching act and this has been attributed to the competition between quenching in the phenyl ring and at the hydridic Si–D bond.[3] Monosilane exhibits a more complex behavior in that hydrogen is formed in a surface-sensitive[1,4-6] chain reaction.

The silyl radicals, common to all these systems, combine to give chemically activated silanes which may either decompose or be pressure stabilized. The thermal decomposition of mono-, di-, and trisilanes proceeds exclusively by the elimination of silylenes to yield silanes.[7,8] The silylene diradicals insert into the substrate to give higher molecular weight silanes.[7-9]

No detailed photochemical study of the disilane molecule has been reported previously. The present investigation was undertaken to obtain information on the mercury photosensitization of disilane and the reactions of disilyl radicals.

Experimental Section

Conventional high-vacuum techniques were used throughout. The 50 × 50 mm cylindrical quartz reaction vessel was surrounded by an aluminum block furnace and attached to a grease-free high-vacuum system. The source of radiation was a Hanovia 687A45 mercury resonance lamp and a Hanovia 30620 medium-pressure mercury arc.

Si_2H_6 and Si_2D_6 (Merck) were distilled before use. Mercury dimethyl (Eastman) was purified by glc. Nitric oxide (Matheson) was distilled at −184° and degassed at −210°. Research grade ethylene (Phillips) and assayed reagent grade hydrogen (Airco) were used without further purification.

Light intensities were determined using propane[10] actinometry, before and after each run because of attenuation of the incident intensity due to polymer deposition on the cell face during a run. The light intensity was in the order of 3×10^{-7} einstein min^{-1}.

Product analyses were performed by glc. H_2, N_2, and CH_4 were measured on a 6-ft 13X molecular sieve column and monosilane, ethane, ethylene, methylsilane, and butane on a medium activity silica gel column. The condensable products were separated on either a 20-ft SE-30 silicone gum rubber on Diatoport S column or on a 10-ft DC200 or DC170 silicon oil on Chromosorb W column. Dimethylmercury was also purified on the latter column.

In the runs with added nitric oxide the condensable products were separated on a 15-ft × $^1/_8$ in. stainless steel column packed with 20% SE-30 on Diatoport S. The Aerograph 1200 Hy-Fi III gas chromatograph was coupled directly to the ion source of an A.E.I. MS12 mass spectrometer.

Results

Mercury Photosensitization of Disilane. The products of the reaction were hydrogen, monosilane, trisilane, *n*-tetrasilane, and a solid polymeric material. Isotetrasilane could have been detected if present since the column employed resolved samples of the two isomeric tetrasilanes.

First the effect of substrate pressure on the product yields was examined. The results are presented in Tables I and II for Si_2H_6 and Si_2D_6, respectively. With the exception of trisilane, all product yields increase with increasing pressure, but the yield of tetrasilane increases more rapidly than that of hydrogen or monosilane. The slow rise in the hydrogen and monosilane yield is caused by the pressure broadening of the resonance line and the attendant increase in the light intensity absorbed. The trend in product yields as a function of pressure becomes more recognizable if the yield ratios ϕ(silane)/ϕ(hydrogen) are plotted against pressure, Figures 1 and 2. It is seen that $\phi(SiH_4)/\phi(H_2)$ is pressure independent, $\phi(Si_3H_8)/\phi(H_2)$ shows a slight de-

---

[1] M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87**, 179 (1965).

[2] (a) J. D. Reedy and G. Urry, *Inorg. Chem.*, **6**, 2117 (1967); (b) J. D. Reedy, *Diss. Abstr. B*, **29**, 924 (1968).

[3] T. L. Pollock, E. Jakubowski, H. E. Gunning, and O. P. Strausz, in preparation for publication.

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

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

[6] (a) H. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964); (b) E. Kamaratos and F. W. Lampe, *ibid.*, 74, 2267 (1970).

[7] W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

[8] I. M. T. Davidson, *Quart. Rev., Chem. Soc.*, **25**, 111 (1971), and references therein.

[9] O. P. Strausz, K. Obi, and W. K. Duholke, *J. Amer. Chem. Soc.*, **90**, 1359 (1968); K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, *ibid.*, **91**, 1622 (1969).

[10] S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 319 (1951).

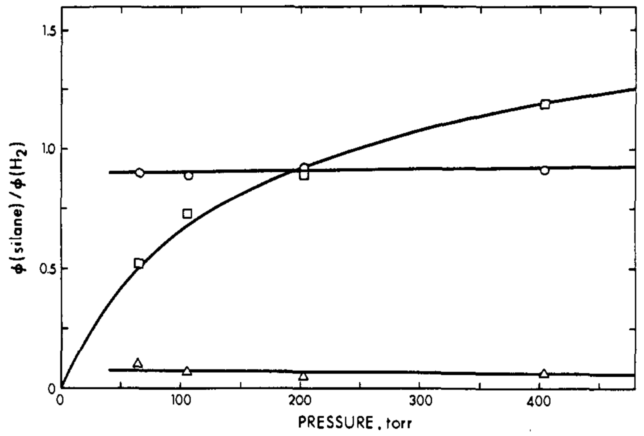

Figure 1. Observed quantum yields of silanes relative to hydrogen *vs.* substrate pressure in the Hg $6(^3P_1)$ sensitized reaction of Si_2H_6 at 25°: (○) SiH_4; (△) Si_3H_8; (□) Si_4H_{10}.

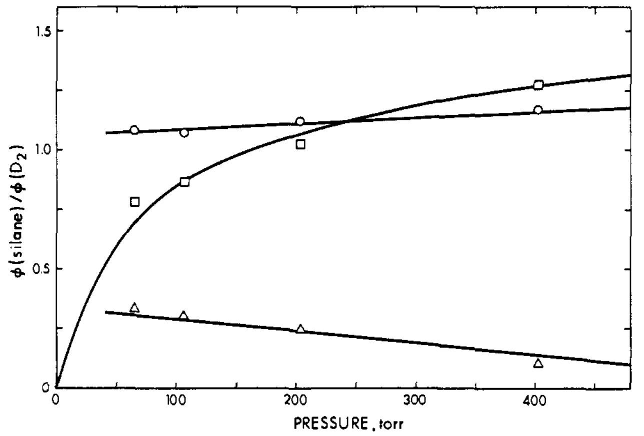

Figure 2. Observed quantum yields of silanes relative to hydrogen *vs.* substrate pressure in the Hg $6(^3P_1)$ sensitized reaction of Si_2D_6 at 25°: (○) SiD_4; (△) Si_3D_8; (□) Si_4D_{10}.

Table I. Product Quantum Yields in the Mercury Photosensitization of Disilane[a]

$P(Si_2H_6)$, Torr	H_2	SiH_4	Si_3H_8	Si_4H_{10}
	φ, mol einstein⁻¹			
404	0.64	0.57		
404	0.63	0.58		
404	0.65	0.58	0.03	0.75
404	0.62	0.54	0.04	0.77
404	0.63	0.56	0.04	0.75
	0.63	0.57	0.04	0.75
202	0.61	0.54	0.03	0.55
202	0.62	0.56	0.03	0.54
	0.62	0.55	0.03	0.55
106	0.54	0.48	0.03	0.39
106	0.55	0.49	0.04	0.41
	0.55	0.49	0.04	0.40
65	0.48	0.44	0.04	0.24
65	0.52	0.45	0.05	0.27
	0.50	0.45	0.05	0.26

[a] Temperature, 25°; photolysis time, 6 min.

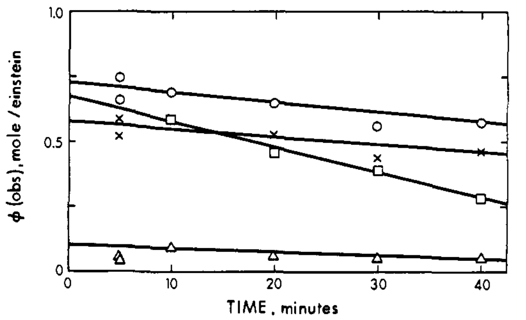

Figure 3. Observed quantum yields of products *vs.* exposure time for the Hg $6(^3P_1)$ sensitized decomposition of Si_2D_6 at 235 Torr of pressure and 25°: (X) D_2; (■) SiD_4; (△) Si_3D_8; (□) Si_4D_{10}.

Table II. Product Quantum Yields in the Mercury Photosensitization of Disilane-d_6[a]

$P(Si_2D_6)$, Torr	D_2	SiD_4	Si_3D_8	Si_4D_{10}
	φ, mol einstein⁻¹			
402	0.57	0.67	0.11	0.73
402	0.59	0.68	0.12	0.78
402	0.61	0.71	0.14	
	0.59	0.69	0.12	0.75
203	0.60	0.66	0.14	0.54
203	0.58	0.67	0.16	0.69
203	0.59	0.66	0.13	0.57
	0.59	0.66	0.14	0.60
106	0.58	0.62	0.17	0.46
106	0.56	0.61	0.17	0.52
	0.57	0.61	0.17	0.49
65	0.52	0.55	0.17	0.41
65	0.51	0.55	0.16	0.38
	0.51	0.55	0.17	0.40

[a] Temperature, 25°; photolysis time, 6 min.

crease and $\phi(Si_4H_{10})/\phi(H_2)$ displays a marked increase with increasing pressure. Deuteration affects the distribution and pressure variation of products only slightly although the yield of the minor product, trisilane, is considerably enhanced. The material balance improves with increasing pressure and at 400 Torr, approximately 90% balance is obtained.

The effect of exposure time was investigated at a Si_2D_6 pressure of 235 Torr. The results, plotted in Figure 3, indicate a significant decline in product yields with increasing irradiation time and this trend is more pronounced for the less stable products, tetrasilane and trisilane. Extrapolation to zero exposure time shows that all four products are of primary origin with initial quantum yields of $\phi(H_2) = 0.66$; $\phi(SiH_4) = 0.59$; $\phi(Si_3H_8) = 0.04$; $\phi(Si_4H_{10}) = 0.86$; $\phi(D_2) = 0.62$; $\phi(SiD_4) = 0.72$; $\phi(Si_3D_8) = 0.13$; $\phi(Si_4D_{10}) = 0.86$, at 25° and 400 Torr pressure.

Since both tetrasilane and hydrogen are major products, an important primary step is probably Si–H bond cleavage

$$Si_2H_6 + Hg^* \longrightarrow Si_2H_5 + H + Hg \qquad (1)$$

by analogy with the reactions of paraffins and methylated silanes. In order to ascertain the presence of H atom in the system the isotopic composition of the hydrogen product was examined from the photosensitization of an equimolar mixture of Si_2H_6 and Si_2D_6. The distribution was in the ratio of $H_2:D_2:HD = 2.4:1.0:2.7$ and consequently it is concluded that reaction 1 is an important primary step. Monosilane may then arise from a simultaneous, competing primary process, or from the secondary reactions of H atoms or disilyl radicals. To clarify this point, the reactions of H atoms with disilane were investigated in auxiliary experiments.

Reaction of H Atoms with Disilane and Monosilane. Hydrogen atoms were produced by the mercury photosensitization of H_2, in the presence of varying amounts of disilane-d_6. The major product of the reaction was monosilane with smaller amounts of trisilane and tetrasilane. The pressure dependence of the product rates is illustrated in Figure 4. Isotopic analysis of the monosilane fraction showed it to consist of SiD_3H and SiD_4, and if isotope effects in the cracking reactions are neglected the minimum concentration of SiD_3H in the mixture is estimated to be about 66%.

These observations dictate a displacement type reaction between hydrogen atoms and disilane

$$H + Si_2D_6 \longrightarrow SiD_3H + SiD_3 \qquad (2)$$

in addition to the more common abstraction reaction

$$H + Si_2D_6 \longrightarrow HD + Si_2D_5 \qquad (3)$$

Since the quantum yield of H-atom production in the mercury photosensitization of H_2 is 2.0,[11] the rate-constant ratio k_2/k_3 is $\sim(0.90 \times 0.66)/(2 - 0.90 \times 0.66) = 0.42$ assuming that $\phi_3 = 2 - \phi(SiD_3H)$. The yield of monosilane is unaffected by temperature in the range 25–220° and it appears that the rate-constant ratio is temperature independent.

Now, combining these results with the quantum yield measurements of hydrogen production from the sensitized decomposition of disilane, the quantum efficiency of primary step 1 turns out to be >0.9 and probably equal to unity and the quantum yields of step 3, from the initial yields of H_2 and D_2, 0.66 and 0.62, respectively. The quantum yields of step 2 are then 0.34 and 0.38.

Next, the nature of the reactions removing the silyl radical was examined. SiH_3 and SiD_3 radicals were generated by the reaction of hydrogen atoms (from the mercury photosensitization of H_2) with an equimolar mixture of SiH_4 and SiD_4 and the resulting disilane, formed with a quantum yield of 0.3, was analyzed for isotopic composition by mass spectrometry. Relying on the published mass spectra of the various deuterated disilanes,[12] the product disilane was found to be composed of isomers containing predominantly an even number of deuterium and hydrogen atoms. This result gives a clear indication that recombination is not an important mode of removing the monosilyl radical from the system and the disilane forms through the intervention of the silylene diradical *via* the sequence

$$H + SiH_4 \longrightarrow H_2 + SiH_3$$

$$H + SiD_4 \longrightarrow HD + SiD_3$$

$$SiH_3 + SiD_3 \longrightarrow SiH_3D + SiD_2$$

$$SiH_3 + SiD_3 \longrightarrow SiH_2 + SiD_3H$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6$$

$$SiH_2 + SiD_4 \longrightarrow Si_2H_2D_4$$

$$SiD_2 + SiH_4 \longrightarrow Si_2D_2H_4$$

$$SiD_2 + SiD_4 \longrightarrow Si_2D_6, \text{ etc.}$$

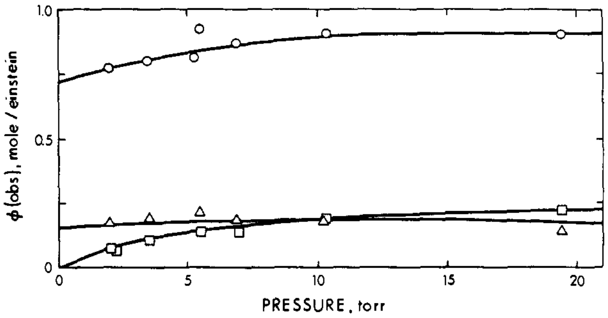

Figure 4. Observed quantum yields of products *vs.* Si_2D_6 pressure for the Hg $6(^3P_1)$ sensitized decomposition of H_2 (H_2:Si_2D_6 = 100:1) at 25°: (○) monosilane; (△) trisilane; (□) tetrasilane.

Reaction of CH_3 Radicals with Disilane. This reaction was investigated in an attempt to produce disilyl radicals without the involvement of hydrogen atoms and to assess the importance of the hypothetical displacement reaction

$$CH_3 + Si_2D_6 \longrightarrow CH_3SiD_3 + SiD_3 \qquad (4)$$

To these ends methyl radicals from the photolysis of dimethylmercury were allowed to react with Si_2D_6 in varying concentrations. The major products were CH_3D and C_2H_6 together with smaller yields of SiD_4, CH_3SiD_3, Si_3D_8, Si_4D_{10}, and about 13 additional methylated silanes present in trace quantities. The low yields of silane products indicate that the disilyl radicals are largely destroyed at room temperature by disproportionation with methyl

$$CH_3 + Si_2D_5 \longrightarrow CH_3D + Si_2D_4, \text{ etc.}$$

From the measured yields of the CH_3SiD_3 product the rate constant of the displacement reaction 4 can be estimated to be at least two orders of magnitude smaller than the rate constant of the abstraction reaction

$$CH_3 + Si_2D_6 \longrightarrow CH_3D + Si_2D_5$$

and therefore it can be concluded that methyl radicals do not behave like hydrogen atoms in group displacement reactions with silicon hydrides.

Effect of Temperature. A cursory study has been made of the effect of temperature on the Hg* + disilane system, the results of which are given in Table III. Up to 210°, the yields of hydrogen and tetrasilane are not affected by temperature, but those of monosilane and trisilane increase in nearly stoichiometric amounts. The steps responsible for the chain processes are most likely the displacement type reaction of the disilyl radicial with the substrate

$$Si_2H_5 + Si_2H_6 \longrightarrow Si_3H_8 + SiH_3 \qquad (5)$$

and the metathetical reaction

$$SiH_3 + Si_2H_6 \longrightarrow SiH_4 + Si_2H_5 \qquad (6)$$

From the Arrhenius plots of the data the apparent activation energies of SiH_4 and Si_3H_8 formation are found to be ~5 and 10 kcal mol^{-1}, respectively.

Scavenging Studies. In order to elucidate the nature of the primary step, and to differentiate between the reactions of monovalent and divalent silicon radicals, scavenging experiments were carried out with ethylene and with nitric oxide.

Ethylene Scavenging. It is known that small amounts of ethylene effectively scavenge silyl radicals with the

---

(11) T. L. Pollock, E. Jakubowski, H. E. Gunning, and O. P. Strausz, *Can. J. Chem.*, 47, 3474 (1969).

(12) M. A. Ring, G. D. Beverly, F. H. Koester, and R. P. Hollandsworth, *Inorg. Chem.*, 8, 2033 (1969).

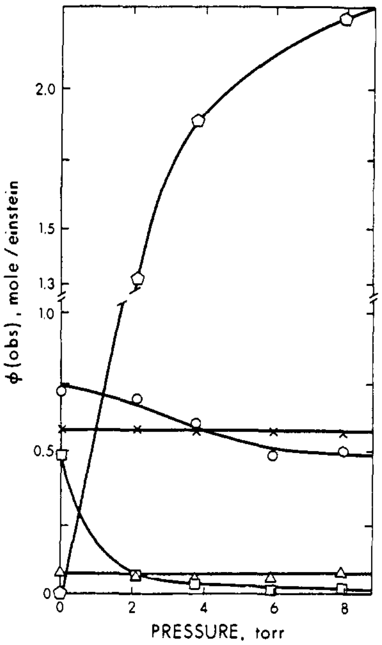

Figure 5. Observed quantum yields of products *vs.* C_2H_4 pressure for the Hg $6(^3P_1)$ sensitization of 200 Torr of Si_2D_6 at 25°: (×) D_2; (○) SiD_4; (△) Si_3D_8; (□) Si_4D_{10}; (⬠) $Si_2D_6C_2H_4$.

Table III. Effect of Temperature on the Mercury Photosensitization of Disilane

Temp, °C	ϕ, mol einstein^{-1} Hydrogen	Monosilane	Trisilane	Tetrasilane
		Si_2H_6[a]		
25	0.63	0.57	0.04	0.75
100	0.64	0.61	0.08	0.68
105	0.58	0.58	0.11	0.62
130	0.63	0.70	0.12	0.65
	0.60	0.67	0.13	0.76
	0.62	0.69	0.13	0.71
161	0.61	0.91	0.40	0.93
	0.60	0.88	0.32	0.74
	0.60	0.87	0.30	0.75
	0.60	0.89	0.34	0.81
178	0.63	1.10	0.51	0.83
	0.59	1.07	0.50	0.77
	0.61	1.09	0.51	0.80
210	0.74	1.75	1.17	0.81
	0.63	1.79	1.09	0.75
	0.69	1.77	1.13	0.78
		Si_2D_6[b]		
25	0.59	0.69	0.12	0.75
207	0.52	1.32	0.71	0.74
	0.68	1.73	0.62	0.70
	0.54	1.24	0.59	0.75
	0.58	1.43	0.64	0.73

[a] $[Si_2H_6] = 2.18 \times 10^{-5}$ mol cm^{-3}. [b] $[Si_2D_6] = 2.14 \times 10^{-5}$ mol cm^{-3}.

production of the 1:1 telomer.[1,5] The results of adding up to 4% ethylene to 200 Torr of Si_2D_6 are shown graphically in Figure 5. The salient features of the reaction may be summarized as follows. (i) The tetrasilane yield is readily suppressed with the simultaneous appearance of the telomer, ethyldisilane, $C_2H_4DSi_2D_5$. The quantum yields of this product rise rapidly with increasing pressure of the added ethylene to values well exceeding unity. (ii) In contrast to the behavior of tetrasilane, the yield of D_2 is unaffected by up to 8 Torr of C_2H_4. The monosilane yield decreases slightly, by about 20% with the appearance of ethylsilane as a minor product. In addition, two heavier products identified as $C_2H_4Si_4D_{10}$ and $C_4H_8Si_4D_{10}$ were also detected in concentrations less than 1% of that of ethyldisilane.

Rate constant values for reactions 2 and 3 were determined by relative rate measurements using reaction

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (7)$$

as reference standard. Hydrogen atoms were produced by the mercury photosensitization of hydrogen in the presence of small concentrations of ethylene and disilane. The results of this study are compiled in Table IV and will be used in calculating the rate constants (*vide infra*).

Table IV. Product Yields from the Mercury Photosensitization of Hydrogen in the Presence of Disilane and Ethylene at 25°[a]

Time, min	Reactant pressure, Torr H_2	Disilane	C_2H_4	Product, μmol Monosilane	Ethane	Butane
			Si_2H_6			
10	400	2.37	5.35	0.60	0.37	0.36
10	400	2.70	9.78	0.36	0.41	0.56
			Si_2D_6			
11	410	2.30	9.60	0.51	0.49	1.38
10	403	2.47	6.08	0.61	0.28	0.75
10	420	2.44	10.12	0.36	0.30	0.90

[a] I_a, 0.23 μeinstein min^{-1}.

Nitric Oxide Scavenging. Finally, a series of experiments was carried out using nitric oxide as scavenger. The results, given in Table V, are similar to those obtained with ethylene as scavenger; addition of 2–3 Torr of NO to 200 Torr of Si_2H_6 drastically suppresses tetrasilane formation and has only a moderate effect on the yields of SiH_4 and Si_3H_8. Among the new products which appear in the system are N_2, N_2O, and five different partially oxidized silicon hydrides. Mass spectral patterns obtained from the isotopically labeled reactant pairs Si_2H_6 + NO, Si_2D_6 + NO, and Si_2D_6 + ^{15}NO on an MS12 high resolution mass spectrometer showed these products to have molecular formulas Si_3H_8O, $Si_3H_8O_2$, $Si_3H_8O_3$, $Si_4H_{10}O_4$, and $Si_4H_{10}O$. Some of these partially oxidized silicon hydrides appear to be unstable at room temperature, and it was observed that $Si_3H_8O_3$ and $Si_4H_{10}O_4$ decompose spontaneously to yield Si_3H_8O and $Si_4H_{10}O$.

Discussion

Primary Process. The results indicate that the sole primary step operative in the mercury photosensitization of disilane is the cleavage of a single Si–H bond

$$Hg^* + Si_2H_6 \longrightarrow Hg + H + Si_2H_5 \qquad (1)$$

This behavior is similar to that established for the primary decomposition of paraffins[13] and methylated

---

(13) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 92.

Table V. Photosensitization of Si_2H_6 in the Presence of NO at 25°[a]

Reactant pressure, Torr Si_2H_6	NO	Product yields, μmol H_2	N_2	N_2O	SiH_4	Si_3H_8	Si_4H_{10}	SiH_3O-Si_2H_5	$SiH_3O(SiH_2O)_3SiH_3$	$(SiH_2O)_4$	$(Si_2H_5)_2O$
200	0	1.37	0	0	1.14	0.033	1.01	0	0	0	0
200	2	*b*	*b*	*b*	*b*	0.040	0.165	*b*	*b*	*b*	*b*
200	2.5	1.77	2.68	2.90	0.70	0.014	0.020	0.592	0.016	0.223	0.212
200	4	2.54	3.08	2.08	0.56	0.033	0.031	1.05	0.062	0.313	0.175
200	5	3.1	3.3	2.6	0.63	*b*	*b*	*b*	*b*	*b*	*b*
200	6	3.23	3.67	2.32	0.62	0.023	0.031	0.601	0.219	0.624	0.098
175	10.0	*b*	*b*	*b*	0.46	*b*	*b*	*b*	*b*	*b*	*b*
175	16.6	*b*	*b*	*b*	0.44	*b*	*b*	*b*	*b*	*b*	*b*

[a] Photolysis time, 10 min. [b] Not determined.

silanes[1] but is in sharp contrast to the mode of decomposition of monosilane where cleavage of more than one bond takes place.[1,6] The transfer of energy is associated with the Si–H bond, and the quenching reaction may be viewed as a simple H-atom abstraction by the excited mercury atom.[14] The quenching cross section of disilane is estimated[15] to be 60–100 Å²; a high value is expected since the hydridic Si–H bonds are excellent hydrogen donors.[16]

The role of Hg $6(^3P_0)$ atoms in the reaction has not been investigated; however, their intervention is unlikely in view of the high quenching cross section for Hg $6(^3P_1)$ atoms. For the same reason band fluorescence from $(Si_2H_6 \cdot Hg^*)$ complexes is also absent.[17]

Overall Mechanism. The nature of products, their quantum yields along with the primary step established and the effect of added scavengers suggest the following steps in the overall reaction

$$H + Si_2H_6 \longrightarrow SiH_4 + SiH_3 \quad \phi = 0.34 \quad (2)$$

$$H + Si_2H_6 \longrightarrow Si_2H_5 + H_2 \quad \phi = 0.66 \quad (3)$$

$$Si_2H_5 + Si_2H_5 \longrightarrow Si_4H_{10}^{\ddagger} \quad (8)$$

$$Si_4H_{10}^{\ddagger} \longrightarrow SiH_2SiH_2 + Si_2H_6 \quad \phi \approx 0.10 \quad (9)$$

$$Si_4H_{10}^{\ddagger} + Si_2H_6 \longrightarrow Si_4H_{10} + Si_2H_6 \quad \phi \approx 0.86 \quad (10)$$

$$Si_2H_5 + Si_2H_6 \longrightarrow Si_3H_8 + SiH_3 \quad \phi \leq 0.04 \quad (5)$$

$$SiH_3 + Si_2H_6 \longrightarrow SiH_4 + Si_2H_5 \quad \phi \approx 0.25 \quad (6)$$

$$Si_2H_5 + SiH_2SiH_2 \longrightarrow Si_2H_6 + Si_2H_3 \quad (11)$$

$$n SiH_2SiH_2 \longrightarrow (SiH_2)_{2n} \quad (12)$$

where the quantum yield values refer to 400 Torr of Si_2H_6.

There is very little known about the chemistry of silyl radicals and especially about their gas-phase combination–disproportionation reactions. The competing combination–disproportionation reactions 10 and 9 of the disilyl radicals are invoked here on the basis of the observed pressure dependence of the tetrasilane product, Figures 1 and 2. Neglecting minor reactions involving the Si_2H_5 radical one can derive the following relation for the pressure dependence of the tetrasilane product.

$$\frac{\phi(H_2)}{\phi(Si_4H_{10})} = \alpha\left(1 + \frac{k_9}{k_{10}}\frac{1}{[Si_2H_6]}\right)$$

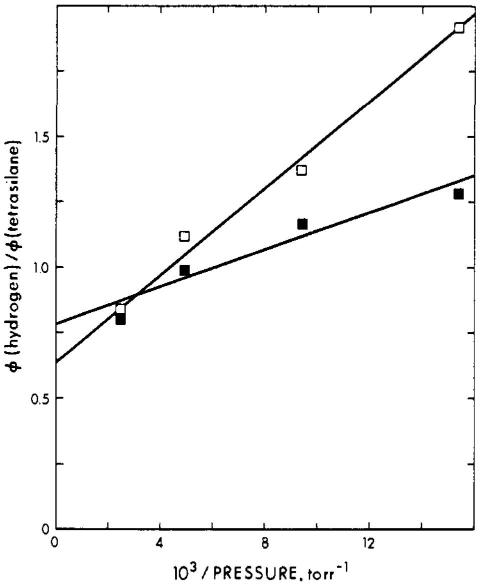

Figure 6. Plot of observed ϕ(hydrogen)/ϕ(tetrasilane) *vs.* reciprocal pressure for the Hg $6(^3P_1)$ sensitized decomposition of disilane at 25°: (□) H_2/Si_4H_{10}; (■) D_2/Si_4D_{10}.

Plotting the yield ratios against the reciprocal pressure of the disilane indeed results in a straight line, Figure 6, the intercept of which gives the extrapolated yield of tetrasilane at infinite pressure, and the slope, with the usual assumption of unit efficiency for the deactivation step, the disproportionation lifetime, 6.2×10^{-10} sec of the chemically activated tetrasilane molecule. For Si_2D_6, the disproportionation lifetime is found to be $\sim 1.5 \times 10^{-9}$ sec which is in line with expectation considering the magnitude of secondary α-H/D kinetic isotope effects. Thus, we arrive at the interesting conclusion that the unimolecular decomposition of the chemically activated tetrasilane yields products, Si_2H_6 + SiH_2SiH_2, analogous to those of the pressure-independent disproportionation of the corresponding carbon radical CH_3CH_2, where disproportionation is considered to take place from a "head-to-tail" collision complex.[18] The alternative mode of disproportionation to give the carbene type radical

$$Si_4H_{10}^{\ddagger} \longrightarrow Si_2H_6 + SiH_3\ddot{Si}H$$

is considered less likely because, from our accumulated experience with silylenes,[9,19] it would be expected to

---

[14] H. E. Gunning, J. M. Campbell, H. S. Sandhu, and O. P. Strausz, *J. Amer. Chem. Soc.*, in press.

[15] A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **41**, 1705 (1964).

[16] O. P. Strausz, E. Jakubowski, H. S. Sandhu, and H. E. Gunning, *ibid.*, **51**, 552 (1969); E. Jakubowski, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *ibid.*, **52**, 4242 (1970); E. R. Morris, and J. C. J. Thynne, *J. Phys. Chem.*, **73**, 3294 (1969).

[17] Unpublished results from this laboratory.

[18] S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

[19] A. G. Alexander and O. P. Strausz, in preparation for publication.

undergo efficient insertion reactions

$$\mathrm{Si_2H_6 + SiH_3\ddot{S}iH \longrightarrow Si_4H_{10}}$$

even at the lowest pressure employed in the present study. On the other hand, the initially formed monosilyl silylene may rearrange to the 1,2 diradical in a very rapid process effectively competing with bimolecular processes. This rearrangement would be energetically favorable and the analogous process

$$\mathrm{SiH_3{-}\ddot{C}H \longrightarrow \dot{S}iH_2{-}\dot{C}H_2}$$

has been shown to completely prevent the insertion of the silyl methylene into the Si–H bond of methylsilane at pressures as high as 400–500 Torr.[9,19] Thus, while at present we favor the mechanism implicating the 1,2 diradical, the precise mode of the disproportionation reaction will have to be assessed from further work currently in progress.

For material balance, in addition to steps 1 and 3, another source of disilyl radicals is necessary. A reasonable possibility is the metathetical reaction 6 of SiH_3 with Si_2H_6.

The displacement-type attack, step 5, of the disilyl radical on disilane as a source of the trisilane product is invoked on the basis of the temperature study. This reaction features an activation energy of the order of 10 kcal mol^{-1} and could possibly account for the small yields of trisilane at room temperature, although the intervention of other processes cannot be excluded with certainty.

The disproportionation reaction 11 of disilyl radicals with the 1,2 diradicals must become important at low pressures where the diradical concentrations are high and the rate of disilyl removal by combination is slow. The polymerization of the diradical, step 12, leads to the formation of the solid deposit. At low pressures it may also serve as a sink for SiH_3 and Si_2H_5 radicals.

Unimolecular Decomposition of Chemically Activated Silanes. It has been shown that the combination product of SiH_3 radicals decomposes in the gas phase below atmospheric pressure. A similar conclusion was drawn also from a study using the triplet mercury photosensitized decomposition of phenylsilane as a source of silyl radicals.[3] This result is expected in view of the observed short lifetime of the chemically activated tetrasilane.

Recent studies of the thermolysis of monosilane and disilane have shown that the energy requirements for decomposition are significantly lower than those necessary for the homolysis of Si–H or Si–Si bonds. The rate coefficient reported[20] for the unimolecular decomposition of Si_2H_6 to $SiH_4 + SiH_2$ is $3.15 \times 10^{14} e^{-48,200/RT}$ sec^{-1}. Now recombination of thermalized monosilyl radicals results in a disilane molecule containing about 85 kcal mol^{-1} excess energy. Therefore chemically activated disilane will decompose *via* this lower energy path very rapidly unless it is collisionally stabilized. We have employed RRKM theory to calculate the unimolecular rate constant k_E for the decomposition of $Si_2H_6^{\ddagger}$ as a function of energy, using the familiar expression

$$k_E = 1^{\ddagger}\left(\frac{I_A^{\ddagger} I_B^{\ddagger} I_C^{\ddagger}}{I_A I_B I_C}\right)^{1/2} \frac{\sum P(E^{\ddagger})}{hN(E_0 + E^{\ddagger})}$$

where the various symbols have the usual significance.[21-23] A rigid activated complex is assumed with vibrations as the only active mode in the reactant and the complex. All vibrations are taken to be harmonic and the moments of inertia ratio of the complex to reactant is taken to be unity. Vibrational frequencies used are those of Bethke and Wilson.[24] The thermal data of Bowrey and Purnell[20] were used to assign frequencies to the activated complex, which are listed in Table VI, together with the reactant assignments. The reaction path degeneracy was taken to be six, and the critical energy computed from the experimental activation energy[20] 46.8 kcal mol^{-1}. Two models of the activated complex were considered; in one, Si–H stretch, and in the other, Si–Si stretch, was taken as the reaction coordinate. The computed rate constants did not differ by more than 10%. $\Sigma(E^{\ddagger})$ and $N(E_0 + E^{\ddagger})$ were evaluated by the method of Whitten and Rabinovitch.[25]

Table VI. Vibrational Frequencies (cm^{-1}) of the Active Molecule and Two Models of the Activated Complex of Disilane

Motion	Molecule	Activated complex model I	II
Si–H stretch	2152, 2154, 2155 2155, 2179 2179	2160(5) Reaction coordinate	2160(6)
SiH_3 bend	909, 844	900(2)	900(2)
SiH_3 deformation	940, 940 929, 929	900(4)	900(4)
SiH_3 rock	379, 379 625, 625	379(2) 625(2)	300(2) 550(2)
Si–Si stretch	434	240(2)	Reaction coordinate
Si–Si torsion	200[a]		150

[a] Assigned considering torsions in $H_3C{-}CH_3$ = 280 cm^{-1} and $H_3Ge{-}GeH_3$ = 144 cm^{-1} (ref 24).

The computed rate constant for Si_2H_6 decomposition at $\langle E \rangle$ = 85 kcal mol^{-1} is 2.0×10^{10} sec^{-1} which requires a half-quenching pressure of about 3 atm. Thus, decomposition to give SiH_4 and SiH_2 will be complete under the experimental conditions employed in this study. The singlet ground-state silylene formed in the reaction will undergo further reactions by either inserting into a silicon–hydrogen bond or terminating at the wall as a unit of polymer.

Combination of Si_2H_5 with SiH_3 and Si_2H_5 will yield chemically activated trisilane and tetrasilane containing 79 and 75 kcal mol^{-1} of energy respectively, estimated from the known and assumed thermochemical data.[26-29] Kinetic parameters for the thermal decomposition of trisilane are not available but it has been

(20) M. Bowrey and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, **321**, 341 (1971).

(21) R. A. Marcus and O. K. Rice, *J. Phys. Chem.*, **55**, 894 (1951); R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952).

(22) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964); B. S. Rabinovitch and M. C. Flowers, *Quart. Rev., Chem. Soc.*, **18**, 122 (1964).

(23) M. C. Lin and K. L. Laidler, *Trans. Faraday Soc.*, **64**, 927 (1968).

(24) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).

(25) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, **38**, 2466 (1963).

(26) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 195.

(27) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961); **68**, 946 (1964).

(28) P. Potzinger and F. W. Lampe, *ibid.*, **73**, 3912 (1969).

(29) Estimated from $D(Si_2H_5{-}H)$ = 90 kcal mol^{-1} and assuming $E_a = 0$ for $H + Si_2H_5 \rightarrow Si_2H_6$.

postulated that the reaction proceeds *via* elimination of silylenes.[30] Information on the thermolysis of tetrasilane is nonexistent. Because of the lack of appropriate data we have used the simple RRK expression $k = A([E - E_0]/E)^{s-1}$ for the tri- and tetrasilane decompositions.

The number of effective oscillators, s, was adjusted to yield the experimental rate constant for the tetrasilane decomposition. Taking $\langle E \rangle = 75$, $E_0 = 44$ kcal mol^{-1}, and $A = 3 \times 10^{14}$ sec^{-1}, s turned out to be less than one-third of the total number of internal degrees of freedom, whereas for paraffins, s, is about one-half. Therefore it appears that silicon bonds are less efficient than carbon bonds in equipartitioning energy, an effect which lies in the opposite direction from that one would expect, considering the frequencies of vibrations.

To compute the rate constant for the decomposition of trisilane, the same fraction of effective oscillators was

$$\mathrm{Si_3H_8}^{\ddagger} \longrightarrow \mathrm{SiH_4} + \mathrm{Si_2H_4}$$

$$\mathrm{Si_3H_8}^{\ddagger} \longrightarrow \mathrm{SiH_2} + \mathrm{Si_2H_6}$$

then employed and similar kinetic parameters assumed. The value obtained, $\sim 10^{11}$ sec^{-1}, is such that the chemically activated trisilane formed by the combination of mono- and disilyl radicals will decompose under the present experimental conditions.

Determination of the Rate Constants, k_2 and k_3. The absolute values of the rate constants can be evaluated from the data in Table IV. Owing to the low pressure of ethylene and disilane present in the system, radical–molecule reactions can be neglected, and it may also be assumed that ethyl radicals only disproportionate with silyl radicals but do not combine. Under these conditions the following reactions prevail in the system.

$$\mathrm{H} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_5} \quad (7)$$

$$\mathrm{C_2H_5} + \mathrm{Si_2H_5} \longrightarrow \mathrm{C_2H_6} + \mathrm{Si_2H_4} \quad (13)$$

$$2\mathrm{C_2H_5} \longrightarrow \mathrm{C_2H_6} + \mathrm{C_2H_4} \quad (14)$$

$$2\mathrm{C_2H_5} \longrightarrow \mathrm{C_4H_{10}} \quad (15)$$

$$\mathrm{H} + \mathrm{Si_2H_6} \longrightarrow \mathrm{SiH_4} + \mathrm{SiH_3} \quad (2)$$

$$\mathrm{H} + \mathrm{Si_2H_6} \longrightarrow \mathrm{H_2} + \mathrm{Si_2H_5} \quad (3)$$

The relative rates of steps 7 and 2 are then given by the relation

$$\frac{R(\mathrm{C_2H_6}) + 2.14R(\mathrm{C_4H_{10}})}{R(\mathrm{SiH_4})} = \frac{k_7(\mathrm{C_2H_4})}{k_2(\mathrm{Si_2H_6})}$$

Taking $k_7 = 6.7 \times 10^{11}$ cm^3 mol^{-1} sec^{-1},[31] the values of k_2 are 6.7×10^{11} and 5.0×10^{11} cm^3 mol^{-1} sec^{-1} for $\mathrm{Si_2H_6}$ and $\mathrm{Si_2D_6}$, respectively. From the ratios of k_2/k_3 obtained from the sensitized decomposition of disilane the values of k_3 are 13.0×10^{11} and 8.1×10^{11} cm^3 mol^{-1} sec^{-1} for $\mathrm{Si_2H_6}$ and $\mathrm{Si_2D_6}$, respectively. This value of k_3 is in reasonable agreement with 33.5×10^{11} cm^3 mol^{-1} sec^{-1} determined in this laboratory employing the photolysis of $\mathrm{C_2D_4}$ as the D atom source.[32]

Apparently both reactions exhibit a direct isotope effect with values of $k_2(\mathrm{H})/k_2(\mathrm{D}) = 1.4$, $k_3(\mathrm{H})/k_3(\mathrm{D}) = 1.6$, $k_3/k_2(\mathrm{H}) = 1.94$, and $k_3/k_2(\mathrm{D}) = 1.63$. This is expected for an abstraction reaction; however, the lack of information concerning the reaction paths of displacement reactions precludes any rationalization of α-isotope effects.

The A factors for the metathetical reactions of methyl and trifluoromethyl radicals with silane are the same as those with the corresponding alkanes.[8,16] Assuming the same holds true for H atoms, the activation energy for reaction 3, taking $\log A = 14.1$, is ~ 3 kcal mol^{-1} which is consistent with the trend observed in the alkane series, *i.e.*, $E_\mathrm{a}(\mathrm{CH_3}) > E_\mathrm{a}(\mathrm{CF_3}) > E_\mathrm{a}(\mathrm{H})$. The activation energies of reactions 2 and 3 appear to be equal since temperature does not affect the yield of $\mathrm{SiH_4}$ up to 200° in the mercury photosensitization of hydrogen and disilane mixtures, and the difference in the rate constant values is due to the difference in the A factors.

Scavenging of Silyl Radicals with Ethylene. To account for the product distribution in these experiments, the following additional reactions are considered.

$$\mathrm{Si_2D_5} + \mathrm{C_2H_4} \longrightarrow \mathrm{Si_2D_5C_2H_4} \quad (16)$$

$$\mathrm{Si_2D_5C_2H_4} + \mathrm{Si_2D_6} \longrightarrow \mathrm{Si_2D_5C_2H_4D} + \mathrm{Si_2D_5} \quad (17)$$

$$\mathrm{Si_2D_5C_2H_4} + \mathrm{Si_2D_5} \longrightarrow \mathrm{Si_2D_5C_2H_4D} + \mathrm{Si_2D_4} \quad (18)$$

$$\mathrm{Si_2D_5C_2H_4} + \mathrm{Si_2D_5} \longrightarrow \mathrm{Si_2D_5C_2H_4Si_2D_5} \quad (19)$$

As mentioned earlier, ethyldisilane is generated in a chain process which is initiated by reactions 1 and 3, propagated by 16 and 17, and terminated by 18 and 19. If reactions 16 and 17 mainly control the steady-state concentration of $\mathrm{Si_2D_5C_2H_4}$ radicals, then

$$[\mathrm{Si_2D_5C_2H_4}] = k_{16}[\mathrm{Si_2D_5}][\mathrm{C_2H_4}]/k_{17}[\mathrm{Si_2D_6}]$$

It is reasonable to assume that the steady-state concentration of disilyl radicals is largely determined by steps 16 to 19 in addition to primary step 1. This then gives

$$[\mathrm{Si_2D_5}]^2 = I_\mathrm{a}k_{17}[\mathrm{Si_2D_6}]/(k_{18} + k_{19})k_{16}[\mathrm{C_2H_4}]$$

A steady-state treatment of reactions 1–3, 8–10, and 16–19 yields

$$\phi^0{}_{\mathrm{Si_4D_{10}}}/\phi_{\mathrm{Si_4D_{10}}} - 1 = \left(1 + \frac{k_3}{k_2 + k_3}\right) \times \left(\frac{k_{18} + k_{19}}{k_8}\right)\frac{k_{16}}{k_{17}}\frac{[\mathrm{C_2H_4}]}{[\mathrm{Si_2D_6}]}$$

where $\phi^0{}_{\mathrm{Si_4D_{10}}}$ is the quantum yield in the absence of ethylene. A plot of the left-hand side of this expression against $[\mathrm{C_2H_4}]$, from the data displayed in Figure 5, yields a straight line from which with $k_{17} \simeq 10^7$ cm^3 mol^{-1} sec^{-1},[33] k_{16} is estimated to be 4×10^9 cm^3 mol^{-1} sec^{-1}. This value is two to three orders of magnitude larger than the corresponding rate constants for alkyl radicals.[34] The enhanced reactivity of the silyl radical toward the double bond may be attributed to greater physical size of the 3p orbital, greater polarizability, and the availability of d orbitals on the silicon atom. In contrast to methyl radicals which are known to be planar,[35] monosilyl radicals retain the tetrahedral con-

---

(30) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969).

(31) An average value of the measurements: W. Braun and M. Lenzi, *Discuss. Faraday Soc.*, No. **44**, 252 (1967); M. C. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **53**, 2776 (1970); J. A. Eyre, T. Hikida, and L. M. Dorfman, *ibid.*, **53**, 1281 (1970); R. D. Penzhorn and B. deB. Darwent, *ibid.*, **55**, 1208 (1970).

(32) K. Obi, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Phys. Chem.*, submitted for publication.

(33) R. E. Berkeley, Ph.D. Thesis, University of Alberta, Edmonton, Canada.

(34) R. J. Cvetanovic and R. S. Irwin, *J. Chem. Phys.*, 46, 1694 (1967).

(35) G. Herzberg, "Molecular Spectra and Molecular Structures. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand, Princeton, N. J., 1966, p 227.

figuration,[36] and this in turn may lower the energy barrier to the addition reaction.

Scavenging of Silyl Radicals with Nitric Oxide. The nature of the reactions between nitric oxide and silyl radicals is largely uncharacterized. Studies reported from this laboratory[1,9,19] have shown that small amounts of nitric oxide suppress the products of silyl radical combinations and that hydrogen, nitrogen, nitrous oxide, and a disiloxane are all formed in a chain reaction. The disiloxane is characteristic of these systems in that the integrity of the primary silyl radical is preserved. The results of this study are similar to those reported earlier in that disilyl dimer, tetrasilane, is suppressed and siloxanes, hydrogen, nitrogen, and nitrous oxide are formed. However, siloxanes containing more than one oxygen atom appear to be formed in reactions involving chain mechanisms. A detailed discussion of this is postponed to a later date.

Thermal Stability of Disilyl Radicals. Information on the thermal stability of unsubstituted silyl radicals is not available. The trimethylsilyl radical is more stable thermally[1] than its hydrocarbon analog, the *tert*-butyl radical, since its unimolecular decomposition was not observed up to 400°. The results of the present study indicate that the silyl radicals, including Si_2H_5, do not decompose up to 220°. Instead the disilyl radical undergoes the novel displacement reaction, $Si_2H_5 + Si_2H_6 \rightarrow Si_3H_8 + SiH_3$, at elevated temperatures. The activation energy, $\sim$10 kcal/mol, estimated for this step is considerably higher than the activation energy of the analogous reaction $H + Si_2H_6 \rightarrow SiH_4 + SiH_3$, which is about 3 kcal/mol.[32] The trend is in line with the accompanying enthalpy changes of the two reactions. Similar displacement-type reactions have recently been reported from other laboratories.[37,38]

Methyl radicals do not engage in displacement reactions with disilane. This correlates with the observation made in the unimolecular decomposition of linear polysilanes[7] that permethylation favors Si–Si homolysis while the presence of α H, halogen, oxygen, or nitrogen favors molecular mode of elimination. The most likely cause of this behavior is the requirement of a bridged structure for the displacement reaction *via* hydrogen bonding of valence-shell expansion and the inability of the methyl group to participate in such bondings.

Finally, the values of the various rate constants determined from the present study are summarized in Table VII.

Table VII. Summary of the Rate Constants Determined from the Present Study

Reaction	k, cm^3 mol^{-1} sec^{-1}
$H + Si_2H_6 \rightarrow SiH_4 + SiH_3$	6.7×10^{11}
$H + Si_2H_6 \rightarrow H_2 + Si_2H_5$	13.0×10^{11}
$H + Si_2D_6 \rightarrow SiD_3H + SiD_3$	5.0×10^{11}
$H + Si_2D_6 \rightarrow HD + Si_2D_5$	8.1×10^{11}
$Si_2D_5 + C_2H_4 \rightarrow Si_2D_5C_2H_4$	4.0×10^{9}

Acknowledgments. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Research Council of Canada for support of the research.

---

(36) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966); J. H. Sharp and M. C. R. Symons, *J. Chem. Soc. A*, 3068 (1970).

(37) J. Spanswick and K. V. Ingold, *Int. J. Chem. Kinet.*, **2**, 1157 (1970).

(38) S. J. Band and I. M. T. Davidson, *Trans. Faraday Soc.*, **66**, 406 (1970).