products. However, step 16 should not be important at high pressure.

Conclusion

The mechanism of ethylene radiolysis by fission recoils has been found to be in general consistent with that elucidated at lower pressures in conventional radiolysis when allowance is made for the increased density and the inhomogeneous energy deposition. The former results primarily in the suppression of the fragmentation of activated intermediates. The latter leads to localized free radical concentrations along the entire track too high to be scavenged by up to 0.75 mol % oxygen.

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References and Notes

(1) B. G. Harvery, *Annu. Rev. Nucl. Sci.*, **10**, 235 (1960).
(2) A. Mozumder, *Advan. Radiat. Chem.*, **1**, 1 (1969).
(3) (a) F. Morse, P. Harteck, and S. Dondes, *Radiat. Res.*, **29**, 317 (1966); (b) P. Harteck and S. Dondes, *Saf. Ser., Int. At. Energy Ag.*, **9** (1960); (c) *Z. Elektrochem.*, **64**, 983 (1960); (d) *J. Chem. Phys.*, **27**, 546 (1957); (e) *Nucleonics*, **15**, 94 (1957).
(4) F. Moseley and A. E. Truswell, AERE-R-3078, 1960.
(5) B. Manowitz and M. Steinberg, BNL 804, 1963.
(6) (a) E. R. White, *Int. J. Appl. Radiat. Isotop.*, **16**, 419 (1965); (b) D. A. Landsman and C. M. Noble, AERE-M-921, 1961.
(7) (a) J. M. Calo, R. C. Axtmann, and R. G. Persing, *Rev. Sci. Instrum.*, **41**, 1639 (1970); (b) J. M. Calo, *Nucl. Sci. Eng.* **42**, 424 (1970); R. Axtmann and J. Sears, *J. Chem. Phys.*, **44**, 3279 (1966).
(8) (a) A. M. Raitsimring, Yu. D. Tsvetkov, and V. M. Moralev, *Int. J. Radiat. Phys. Chem.*, **5**, 249 (1973); (b) L. A. Bulanov, E. V. Starodubtseva, and E. A. Borisov, *Khim. Vys. Energ.*, **6**, 476 (1972).
(9) J. W. Boyle, C. J. Hochandel, T. J. Sworski, J. A. Ghormey, and W. F. Kieffer, *Proc. Int. Conf. Peaceful Uses At. Energy*, **1**, 576 (1955).
(10) A. W. Boyd and H. W. J. Conner, *Can. J. Chem.*, **42**, 1418 (1964).
(11) A. W. Boyd and O. A. Miller, *Can. J. Chem.*, **46**, 3773 (1968).
(12) M. Steinberg, W. Tucker, and G. Farber, BNL 10998-R, 1967.
(13) M. Steinberg, BNL 804, 1963.
(14) (a) C. Willis, A. W. Boyd, and D. A. Armstrong, *Can. J. Chem.*, **47**, 3783 (1969); (b) R. E. Rebbert, S. G. Lias, and P. Ausloos, *J. Res. Nat. Bur. Stand., Sect. A*, **77**, 249 (1973).
(15) F. Seitz and J. S. Koehler, "Solid State Physics," Vol. II, F. Seitz and D. Turnbull, Ed., Academic Press, New York, N. Y., 1956, p 35.
(16) G. G. Meisels, J. P. Freeman, and J. P. Gregory, *J. Phys. Chem.*, submitted for publication.
(17) (a) M. C. Sauer and L. M. Dorfman, *J. Phys. Chem.*, **66**, 322 (1962); (b) *J. Chem. Phys.*, **35**, 497 (1961).
(18) (a) G. G. Meisels, *J. Amer. Chem. Soc.*, **87**, 950 (1965); (b) *Trans. Amer. Nucl. Soc.*, **7**, 308 (1964); (c) *J. Chem. Phys.*, **42**, 2328 (1965); (d) *ibid.*, **42**, 3237 (1965); (e) G. G. Meisels and T. J. Sworski, *J. Phys. Chem.*, **69**, 815 (1965); (f) *ibid.*, **69**, 2867 (1965).
(19) (a) J. Gawlowski and J. Niedzielski, *Int. J. Radiat. Phys. Chem.*, **5**, 419 (1973); (b) J. Niedzielski and J. Gawlowski, *ibid.*, **5**, 239 (1973); (c) *Nukleonika*, **15**, 531 (1970); (d) *Radiochem. Radioanal. Lett.*, **2**, 291 (1969); (e) *Nukleonika*, **16**, 143 (1971).
(20) (a) G. G. Meisels, *Advan. Chem. Ser.*, **58**, 243 (1966); (b) G. G. Meisels, "Organic Gases" in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968.
(21) W. H. Wahl and G. G. Meisels, *Rev. Sci. Instrum.*, **36**, 508 (1965).
(22) J. Gawlowski, J. Niedzielski, and A. Bierzynski, *Chem. Anal. (Warsaw)*, **15**, 721 (1970).
(23) (a) There exists a slight difference in dose between the N_2O and the C_2H_4 experiments due to fuel foil differences. In the radiolysis of N_2O the primary irradiation capsules utilized larger foil. The ethylene radiolysis utilized smaller fuel foil and consequently the dose is smaller. (b) W. C. Richardson and G. G. Meisels, to be published.
(24) (a) J. A. Miller, "Combustion" in "Ethylene and Its Industrial Derivatives," J. A. Miller, Ed., Benn Limited, London, 1969; (b) K. Goldman, *ibid.*, "The Physical Properties of Ethylene."
(25) J. V. Michael, D. T. Osborne, and G. N. Suess, *J. Chem. Phys.*, **68**, 2800 (1971).
(26) For recent compilations of pertinent kinetic data see the following comprehensive articles: (a) J. A. Kerr, "Rate Processes in the Gas Phase," in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973; (b) M. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973), and references therein.
(27) (a) P. T. Holland and J. A. Stone, *Can. J. Chem.*, **52**, 348 (1974); (b) H. H. Carmichael, R. Gordon, Jr., and P. Ausloos, *J. Chem. Phys.*, **42**, 343 (1965); (c) C. M. Wodetzki, P. A. McCusker, and D. B. Peterson, *J. Phys. Chem.*, **69**, 1056 (1965).
(28) L. C. Northcliffe and R. F. Schilling, *Nucl. Data, Sect. A*, **7**, 233 (1970).
(29) R. A. Holroyd and R. W. Fessenden, *J. Phys. Chem.*, **67**, 2743 (1963).
(30) T. O. Tiernan and J. H. Futrell, *J. Phys. Chem.*, **72**, 3080 (1968).
(31) C. Willis, O. A. Miller, A. E. Rothwell, and A. W. Boyd, *Advan. Chem. Ser.*, **No. 81**, 539 (1968).
(32) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).
(33) P. G. Clay and A. A. Siddiqi, *Chem. Commun.*, 1271 (1969).

Kinetics of the Thermal Decomposition of Methyldisilane and Trisilane

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Abstract: The kinetics of the gas-phase thermal decomposition of methyldisilane and trisilane in the temperature ranges 539.6–569.6°K and 529.6–560.5°K, respectively, are reported. Rate constants for the homogeneous, unimolecular initial decomposition reactions as shown are ($\theta = 2.3RT$): $CH_3Si_2H_5 \rightarrow SiH_2 + CH_3SiH_3$ ($\log k(\mathrm{sec}^{-1}) = (15.28 \pm 0.15) - (50.75 \pm 0.36)/\theta$); $CH_3Si_2H_5 \rightarrow CH_3SiH + SiH_4$ ($\log k(\mathrm{sec}^{-1}) = (14.14 \pm 0.14) - (49.89 \pm 0.35)/\theta$); $Si_3H_8 \rightarrow SiH_2 + Si_2H_6$ ($\log k(\mathrm{sec}^{-1}) = (15.69 \pm 0.18) - (52.99 \pm 0.43)/\theta$); $Si_3H_8 \rightarrow SiH_3SiH + SiH_4$ ($\log k(\mathrm{sec}^{-1}) = (14.68 \pm 0.23) - (49.24 \pm 0.55)/\theta$). It is argued that the relatively low activation energies observed support 1,2-H migration *via* hydrogen-atom bridged transition states, and that the relatively high A factors observed indicate that these transition states are quite "loose." Other derived thermodynamic and kinetic data are reported, including a value for the heat of formation of methyldisilane, $\Delta H_f°(CH_3Si_2H_5) = 12.6$ kcal/mol; heats of formation of the product silylenes, $\Delta H_f°(SiH_2) = 58.6 \pm 3.5$ kcal/mol; $\Delta H_f°(CH_3SiH) = 50.9 \pm 3.5$ kcal; $\Delta H_f°(SiH_3SiH) = 64.5 \pm 3.5$ kcal/mol; and A factors for these silylene insertion reactions (*i.e.*, the reverse of the decomposition reactions studied). Silylene insertions into (Si–C) and (C–H) bonds were not observed. Insertions into (Si–Si) bonds are argued to be inconsistent with the present data.

Initiation reactions in the thermal decompositions of saturated hydrocarbons are with no exceptions (C–C) or (C–H) bond fission reactions. Similarly, an (Si–H) bond rupture appears to be the initial step in the silane (SiH_4) thermal decomposition.[1] However, Si_2H_6,[2-4] $CH_3Si_2H_5$,[5] 1,2-$(CH_3)_2Si_2H_4$,[5] $(CH_3)_5Si_2H$,[6] and Si_3H_8[2,7] decompose *via* 1,2-hydrogen shift reactions to form silanes and silylenes,[2-7] (*cf.* reaction 1) where R represents H, SiH_3, or CH_3. This

$$R_3SiSiHR_2 \longrightarrow R_3SiH + SiR_2 \qquad (1)$$

type of elimination reaction is only observed in high energy (vacuum uv) photochemical decompositions of hydrocarbons.[8] That 1,2-hydrogen shift reactions occur in polysilane thermal decompositions, but not in hydrocarbon pyrolyses, can probably be attributed to the availability of low-lying nonoccupied orbitals (4s and 3d) on silicon which can provide appreciable bonding stabilization for pentavalent silicon in the transition state, and to the relative stability of divalent silicon. Since both these properties are enhanced as one proceeds down through the group IV metals, 1,2-hydrogen shift reactions are expected to dominate the thermal decompositions of polygermanes, polyplumbanes, and polystananes. In fact the initial reaction in the thermal decomposition of digermane appears to be a 1,2-hydrogen shift forming germane and germylene.[3] Thus, as is so often the case, the chemistry of the first-row elements (in this case carbon) is the exception rather than the rule.

It is interesting to note that 1,2-migration followed by silylene elimination is not confined to H atoms. Methoxydisilanes and halogenated polysilanes decompose *via* 1,2-methoxy group[9] shifts and halogen[10] atom shifts.

Until this study, disilane was the only polysilane containing (Si-H) bonds whose thermal decomposition kinetics has been studied.[11] The Arrhenius parameters obtained for the 1,2-hydrogen shift reaction 1b of that study provided the

$$Si_2H_6 \longrightarrow SiH_4 + SiH_2 \tag{1b}$$

$$\log k(\text{sec}^{-1}) = 14.5 - 49.3/\theta$$

sole quantitative measurement for a member of this potentially very important class of reactions. We report here the kinetics of the thermal decompositions of two more polysilanes: trisilane and methyldisilane. This research was undertaken to extend the kinetic data on 1,2-hydrogen shift reactions in molecules, and to examine *via* the kinetics the nature and structure of the transition states involved. Microscopic reversibility, then, assures corresponding information about the chemically more common singlet silylene insertion reactions.

The series of reactants for which data are now available, namely disilane, methyldisilane, and trisilane (*i.e.*, Si_2H_5R, where R = H, CH_3, and SiH_3, respectively), is particularly interesting in that the results provide information on the effect of varying R group substituents on substituted disilane stabilities.

Experimental Section

Kinetics of the gas phase decomposition reactions were studied in a grease free high vacuum system by the static method. Walls of the vacuum line were treated with $(CH_3)_3SiCl$ which renders them relatively inert. Inner walls of the reaction cell, volume ≈ 386 cm^3, were deactivated by decomposing SiH_4 in the reaction cell at 400° and then evacuating at this temperature for 24 hr. This procedure generates a silicon mirror *via* the breakdown of the polymeric reaction product of the silane decomposition. Bowery and Purnell[11] found no surface dependence for the disilane decomposition over a silicon mirror surface. Our results for trisilane and methyldisilane parallel this result.

Temperatures of the reaction cell were maintained and controlled constant to within ±0.1° using a well insulated, air stirred, electric furnace in conjunction with a proportional temperature controller (Bayley Instruments Co., Model 124). Temperatures were measured potentiometrically (L and N-K3) with a calibrated chromel-alumel thermocouple.

Products and reactants were routinely identified by infrared spectroscopy (Perkin-Elmer Model 337) and by mass spectroscopy (Hitachi Model RMU-6E). Reactant and product concentrations in the kinetic runs were followed quantitatively relative to an inert internal standard: tetramethylsilane, TMS, using gas-liquid chromatography (Carle Model 8004 thermal conductivity chromatograph and a Varian Model A-25 recorder equipped with a disk integrator). Analysis of the reactants and "light" products were made with an 8% Squalene on Supelcaport 24 ft stainless steel column, or with an 8% G.E. SF96 (silicone) 90-100 mesh Anakrom ABS 18 ft stainless steel column. For heavier reaction products (*i.e.*, Si_4H_{10} and Si_5H_{12}) a 6 ft SF96 column was used. Column temperatures were adjusted from 25 to 200°, while the detector temperature was fixed at 200°. Chromatographic methods of silane analyses are described in detail elsewhere.[12]

Trisilane was prepared from the flow pyrolysis of disilane as described by Tebben and Ring.[2] Methyldisilane was prepared from the flow pyrolysis of disilane in the presence of a large excess of methylsilane.[5] After vacuum distillation, and separation from other reaction products, these compounds were found to be better than 99% pure by glpc analysis. The internal standard, TMS, obtained from Ventron, was 99.5% pure as on determined by glpc.

To avoid complications due to secondary reactions of products, the kinetics of decomposition were followed only over the first 5% of reaction. Thus kinetic constants correspond closely to initial reaction rates.

Results

Methyldisilane, studied in the temperature range from 539.6 to 569.6°K, decomposes to silane, methylsilane, 1- and 2-methyltrisilane, and 1,2- and 1,3-dimethyltrisilane. In prior investigations[3,5] we have demonstrated that formations of these products undoubtedly occur *via* primary reactions 2 and 3 and secondary insertion reactions 4s, 4p, 5s, and 5p as shown below.

primary

$$CH_3Si_2H_5 \longrightarrow SiH_2 + CH_3SiH_3 \tag{2}$$
$$CH_3Si_2H_5 \longrightarrow CH_3SiH + SiH_4 \tag{3}$$

secondary

$$SiH_2 + CH_3Si_2H_5 \longrightarrow 2\text{-}CH_3Si_3H_7 \tag{4s}$$
$$SiH_2 + CH_3Si_2H_5 \longrightarrow 1\text{-}CH_3Si_3H_7 \tag{4p}$$

$$CH_3SiH + CH_3Si_2H_5 \longrightarrow 1,2\text{-}(CH_3)_2Si_3H_6 \tag{5s}$$
$$CH_3SiH + CH_3Si_2H_5 \longrightarrow 1,3\text{-}(CH_3)_2Si_3H_6 \tag{5p}$$

Trisilane, studied in the temperature range 529.6-560.5°K, decomposes to disilane, normal and isotetrasilane, and normal and isopentasilane. The pertinent primary and secondary reactions for this system are represented by reactions 6-9.[7]

In reactions 4, 5, 8, and 9, s refers to an insertion into the central or secondary Si-H bond and p refers to an insertion into terminal or primary Si-H bonds.

primary

$$Si_3H_8 \longrightarrow SiH_2 + Si_2H_6 \tag{6}$$
$$Si_3H_8 \longrightarrow SiH_3SiH + SiH_4 \tag{7}$$

secondary

$$SiH_2 + Si_3H_8 \longrightarrow i\text{-}Si_4H_{10} \tag{8s}$$
$$SiH_2 + Si_3H_8 \longrightarrow n\text{-}Si_4H_{10} \tag{8p}$$

$$SiH_3SiH + Si_3H_8 \longrightarrow i\text{-}Si_5H_{12} \tag{9s}$$
$$SiH_3SiH + Si_3H_8 \longrightarrow n\text{-}Si_5H_{12} \tag{9p}$$

Kinetic data are listed in Tables I and II. Table III illustrates experimentally determined product and reactant pressures as a function of time for a representative run at each temperature examined in this study. The decomposition kinetics of both methyldisilane and trisilane were found to be first order. Thus two- to threefold variations in reactant concentrations ($CH_3Si_2H_5$ from 26 to 60 mm, Si_3H_8 from 37 to 104 mm) produced corresponding variations in reactions rates. First-order rate constants (Tables I and II, columns 4 and 5) derived from primary product formations are within experimental error unaffected by variations in

Table I. Data on the Pyrolysis of Methyldisilane

Run no.	Initial pressure[a] P_0(CH_3-Si_2H_5)	Total pressure[b] P_0(total)	Rate constants ($sec^{-1} \times 10^6$) for product formation SiH_4	CH_3SiH_3
		T = 539.9°K		
1	66	132	0.851	5.35
2	66	159	0.877	5.47
3	71	161	0.878	5.55
		T = 549.4°K		
4	60	105	1.91	12.0
5	56	119	1.94	12.3
6	33	53	1.95	12.3
7	26	47	1.95	12.3
		T = 553.0°K		
8	59	174	2.93[c] (2.63)	1.94[c] (16.6)
9	66	187	3.22[c] (2.63)	20.1[c] (16.6)
		T = 560.0°K		
10	65	125	4.52	29.3
11	67	131	4.48	28.4
12	68	160	4.43	28.4
		T = 569.5°K		
13	75	125	10.2	66.1
14	68	119	9.83	64.6
15	70	119	9.70	63.8

[a] Pressure in mm. [b] $P_0(\text{total}) \simeq P_0(CH_3Si_2H_5) + P_0(\text{TMS})$ in mm. [c] Surface/volume ratio increased from 1.0 to 12.1 cm^{-1}. Values in parentheses are those calculated from the Arrhenius parameters derived from a least-squares analysis of the observed rate constants for runs in the unpacked reaction vessel.

Table II. Data on the Pyrolysis of Trisilane

Run no.	Initial pressure[a] P_0(Si_3H_8)	Total pressure[b] P_0(total)	Rate constants ($sec^{-1} \times 10^6$) for product formation SiH_4	Si_2H_6
		T = 529.6°K		
16	62	82	2.15	0.619
17	57	81	2.20	0.667
18	59	97	2.24	0.679
19	64	92	2.43	0.652
		T = 535.7°K		
20	104	105	4.04	1.26
21	36	37	4.04	1.26
22	58	97	3.63	1.05
		T = 540.1°K		
23	60	102	5.56	1.81
24	63	123	5.53	1.72
25	62	65	6.19	1.71
		T = 550.3°K		
26	82	122	14.2	4.23
27	77	126	13.3	4.44
28	57	91	13.0	4.60
		T = 557°K		
29	60	65	26.1[c] (23.4)	7.17[c] (7.59)
30	69	76	17.0[c] (23.4)	6.11[c] (7.59)
		T = 560.3°K		
31	59	97	30.9	10.6
32	68	99	29.4	10.4
33	58	97	30.3	10.8

[a] Pressure in mm. [b] $P_0(\text{total}) = P_0(Si_3H_8) + P_0(\text{TMS})$ in mm. [c] Surface/volume ratio increased from 1.0 to 12.1 cm^{-1}. Values in parentheses are those calculated from the Arrhenius parameters derived from a least-squares analysis of the observed rate constants for runs in the unpacked reaction vessels.

Table III. Reactant and Product Pressures[a] as a Function of Time

Run no.	Time, sec	Pressure, mm		
		$CH_3Si_2H_5$	SiH_4	CH_3SiH_3
Table I				
2	0	66.0		
	1841	64.4	0.123	0.772
	2691	64.2	0.176	1.12
	3613	62.2	0.225	1.41
	4641	63.4	0.297	1.86
	5436	61.5	0.337	2.11
5	0	56.0		
	662	54.6	0.086	0.544
	1058	55.4	0.126	0.800
	1580	55.5	0.189	1.20
	2026	55.1	0.241	1.53
	2557	53.3	0.295	1.87
9	0	66.0		
	891	61.7	0.230	1.49
	1143	62.2	0.282	1.82
	1452	61.0	0.349	2.25
	1731	59.0	0.420	2.71
	1980	57.9	0.468	3.02
11	0	67.0		
	557	65.0	0.204	1.30
	938	65.1	0.326	2.08
	1159	63.3	0.390	2.49
	1396	61.7	0.471	3.00
	1651	61.5	0.551	3.51
14	0	68.0		
	311	66.0	0.259	1.69
	561	65.8	0.447	2.93
	742	63.3	0.533	3.51
	957	62.2	0.724	4.75

Run no.	Time, sec	Pressure, mm		
		Si_3H_8	SiH_4	Si_2H_6
Table II				
18	0	59.0		
	4810	58.4	0.498	0.161
	6969	56.4	0.753	0.240
	9044	57.3	0.998	0.310
	11121	56.5	1.20	0.376
20	0	104.0		
	1865	101.8	0.732	0.253
	3030	102.8	1.23	0.400
	4424	103.4	1.78	0.535
	5532	98.6	2.18	0.712
	6745	100.6	2.83	0.900
24	0	63.0		
	2106	60.8	0.595	0.200
	3007	60.1	0.818	0.278
	3905	59.9	1.12	0.361
	4851	58.0	1.39	0.451
27	0	77.0		
	880	74.5	0.770	0.263
	1215	73.0	1.09	0.363
	1648	71.3	1.46	0.493
	1990	70.9	1.74	0.570
	2287	69.8	2.01	0.686
29	0	60.0		
	1438	57.6	1.79	0.598
	1715	57.7	2.33	0.732
	2103	55.8	2.85	0.890
32	0	68.0		
	372	66.2	0.667	0.241
	568	64.9	1.02	0.364
	775	64.5	1.37	0.480
	946	63.2	1.67	0.596

[a] Pressures have been adjusted to account for decrease in total pressure resulting from aliquot sampling.

total pressure (P(total) varied over a twofold range), and unaffected by variations in surface to volume ratios ($S/V \simeq$ 1 cm^{-1} in most runs; $S/V \simeq$ 12.1 cm^{-1} in runs 8, 9, 29, and 30). Therefore, the primary dissociation reactions (reactions 2, 3, 6, and 7) are homogeneous, unimolecular processes in their high-pressure region. Arrhenius parameters for these reactions, determined from least-square analyses of the rate constants in the Arrhenius equation, $\ln k = \ln A - E/RT$, are listed in Table IV.

Data for the silylene insertion reactions are given in

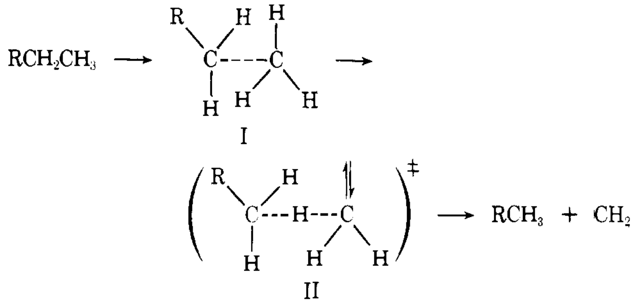


Figure 1. Pictorial representation of the 1,2-H-shift decomposition mode in hydrocarbons.

Table V. For all three silylenes (SiH_2:, CH_3SiH:, and SiH_3SiH:), insertion into the available (Si-H) bonds is close to statistical. Thus for SiH_2: and CH_3SiH: insertions into $CH_3SiH_2SiH_3$, the relative rates of insertion into the three primary Si-H bonds compared to the two secondary (Si-H) bonds are 1.41 and 1.30, respectively (*i.e.*, only slightly less than the statistical value of 1.5). Similarly, the rates of SiH_2: and SiH_3SiH: insertions into the primary *vs.* secondary (Si-H) bonds of trisilane are 3 within experimental error. Insertion into the (C-H) bonds of methyldisilane was *not* observed. Comparisons of the yields of insertion products to the yields of primary dissociation extrapolated to zero reaction time indicate that the silylenes are not quantitatively trapped *via* insertion reactions. Thus the per cent insertion ranges from a low of 40 ± 10% for Si_2H_4 insertion into trisilane, to values very close to 70% for the insertions of SiH_2 and CH_3SiH. The lower insertion product yields for the Si_2H_4 species may well be a result of some isomerization to the very unstable (to polymerization) molecular species, $H_2Si{=}SiH_2$. Polymer formation is very likely the fate of all silylene species not "trapped" by insertion reactions.

The insertion ratios and product yields of this study are in reasonable agreement with those obtained in a prior study[7] in which heavy insertion products were cold trapped and removed from a Toepler pumped circulating reaction stream. The ratios of that study are shown in parentheses in Table V.

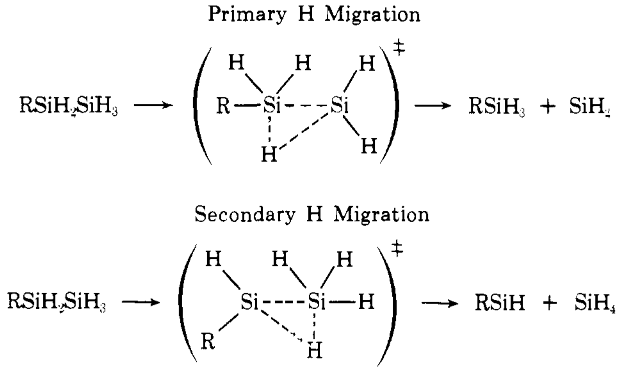


Figure 2. Pictorial representations of the 1,2-H-shift decomposition reactions of polysilanes.

Table IV. Arrhenius and Transition State Parameters[a,b] for Primary Formation in the Pyrolysis of Methyldisilane and Trisilane

Methyldisilane

Reaction 2

$CH_3Si_2H_5 \xrightarrow{2} SiH_2{:} + CH_3SiH_3$

$\log k_2(\sec^{-1}) = (15.28 \pm 0.15) - (50.75 \pm 0.36)/\theta$

$\Delta S_2^* = 8.3 \pm 0.8$ eu; $\Delta H_2^* = 49.70 \pm 0.36$ kcal

Reaction 3

$CH_3Si_2H_5 \xrightarrow{3} {:}\,SiHCH_3 + SiH_4$

$\log k_3(\sec^{-1}) = (14.14 \pm 0.14) - (49.89 \pm 0.35)/\theta$

$\Delta S_3^* = 3.1 \pm 0.8$ eu; $\Delta H_3^* = 48.86 \pm 0.43$ kcal

Trisilane

Reaction 6

$Si_3H_8 \xrightarrow{6} {:}SiH_2 + Si_2H_6$

$\log k_6(\sec^{-1}) = (15.69 \pm 0.18) - (52.99 \pm 0.43)/\theta$

$\Delta S_6^* = 10.1 \pm 0.8$ eu; $\Delta H_6^* = 51.93 \pm 0.43$ kcal/mol

Reaction 7

$Si_3H_8 \xrightarrow{7} {:}SiHSiH_3 + SiH_4$

$\log k_7(\sec^{-1}) = (14.68 \pm 0.23) - (49.24 \pm 0.55)/\theta$

$\Delta S_7^* = 5.5 \pm 1.0$ eu; $\Delta H_7^* = 48.17 \pm 0.55$ kcal

[a] $\log k(\sec^{-1}) = \log A(\sec^{-1}) - E(\text{kcal})/\theta$, where $\theta = 2.3RT$ (in kcal). [b] $\ln A = \ln(ek\bar{T}/h) + (\Delta S^*/R)$; $E = \Delta H^* + R\bar{T}$; $\bar{T}$ = mean reaction temperature.

Discussion

Unimolecular Decompositions of Methyldisilane and Trisilane. By examining the energetics of methylene insertion into a (C-H) bond in methane, calculations by Dobson, Hayes, and Hoffmann[13] indicate that the transition state for this process (and therefore also for the reverse 1,2-H-shift decomposition of ethane) resembles an H-abstraction reaction by methylene, as originally suggested by Benson.[14,15] The reverse methylene elimination reaction path, then, can be pictured as shown in Figure 1.

Note that elimination proceeds through a conformation which strongly resembles the transition state for bond rupture to radical fragments (I), and that the transition state for methylene elimination (II) must lie at a higher energy than this conformation. Dobson, Hayes, and Hoffman calculate a small (but apparently operationally very significant) energy difference between II and I of about 7 kcal.[13]

By contrast, silylene elimination reactions have activation energies which are much lower than (Si-Si) bond energies: E_{act} ($Si_2H_6 \rightarrow SiH_2 + SiH_4$) = 49.3 kcal/mol;[11] $DH°$ (SiH_3-SiH_3) = 84 or 81 kcal/mol.[16] Hence silylene eliminations, on energy grounds, cannot proceed *via* methylene elimination type reaction paths. The alternative path for methylene elimination, with a transition state involving a 1,2-H shift and pentavalent carbon, is apparently not energetically feasible in hydrocarbon reactions because of the high energies of the lowest unoccupied orbitals on carbon. However, for silanes, such a reaction path seems very reasonable. The silylene elimination reaction path, then, is probably as depicted in Figure 2. Note that a rehybridization from sp^3 bonding in the reactant to something resembling dsp^3 bonding at the acceptor silicon center of the tran-

Table V. Insertion Data (530–570°K)[a]

$CH_3Si_2H_5$ reaction	Product ratio (k_p/k_s)[b]	Per cent insertion[c]
$CH_3Si_3H_7$	1.41 ± 0.04	74 ± 2
$(CH_3)_2Si_3H_6$	1.30 ± 0.02	71 ± 2
Si_3H_8 reaction		
Si_4H_{10}	3.5 ± 0.4[d] (3.7)	72 ± 8 (~80)
Si_5H_{12}	2.8 ± 0.4[d] (2.1)	40 ± 10 (~30)

[a] No observable temperature effect on the ratio k_p/k_s was found. [b] k_p is insertion at a terminal or primary Si–H bond while k_s is insertion at a secondary Si–H bond. [c] Products are formed by insertion of SiH_2, CH_3SiH, or SiH_3SiH inserting into $CH_3Si_2H_5$ or Si_3H_8. [d] Because analyses for Si_4H_{10} and Si_5H_{12} were difficult, data on the insertion reactions producing these products were not routinely obtained, hence the larger uncertainties associated with these data.

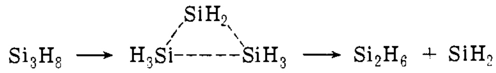
sition state (*i.e.*, participation of pentavalent silicon) is required.

An examination of the rate constants and Arrhenius parameters for the two possible 1,2-H-shift reaction modes of methyldisilane and trisilane indicates that in the temperature range of study the primary H-shift reaction to form methylsilane (reaction 2) is the preferred reaction for methyldisilane and the secondary H-shift reaction to form silane (reaction 7) is the preferred reaction for trisilane. These relative rate results seem to involve an interesting balance between the activation entropy and energy requirements. Thus the activation energies for primary H-1,2 migrations are higher than the competitive secondary H-atom migrations by 1 to 3 kcal (for $CH_3Si_2H_5$ and Si_3H_8, respectively), but the *A* factors for primary H migrations are also higher by close to an order of magnitude in both cases.

It is interesting to note that the observed activation energies seem to correlate with the difference in the (Si-H) bond dissociation energies of the "breaking" and "forming" bonds in the 1,2-H migrations. Thus, assuming a correlation between Si-H stretching frequencies and (Si-H) bond dissociation energies,[17] we suggest the following order for the latter: $DH°$ (SiH_3-H) > $DH°$ (CH_3SiH_2-H) > $DH°$ (SiH_3SiH_2-H) ≃ $DH°$ ($Si_2H_5SiH_2$-H) > $DH°$ ($SiH_2(CH_3)SiH$-H) > $DH°$ ($(SiH_3)_2SiH$-H). This is a "normal" sequence in which both silyl and alkyl substitutions on silicon weaken the remaining Si-H bonds, and silyl substitution effects the greater dissociation energy reduction. The expected order for the activation energies of the 1,2-H migration, then, is as observed, $E_6 > E_2 > E_3 > E_7$, with the highest value of 53 kcal for reaction 6 (in which a primary Si-H bond is broken and the weakest of the secondary Si-H bonds is formed), and the lowest value of 49.2 kcal for reaction 7 (in which the weakest of the secondary Si-H bonds is broken and a primary Si-H bond is formed).

It is also interesting to note both the relatively large positive activation entropies for all four of the dissociation reactions,[18] and the noticeably higher activation entropies of the primary 1,2-H migration reactions (*i.e.*, reactions 2 and 6). These reactions have activation entropies about 5 eu larger than their competing secondary H-migration decomposition modes. We have been able to rationalize these remarkable entropy observations through transition state thermochemical estimates[19] (*i.e.*, *A* factor estimates to within a factor of 2),[20] but only by proposing sizable reductions in the bending, stretching, and rocking modes associated with the separating silicon centers. Rehybridization to pentavalent silicon for the acceptor silicon center is proposed to effect additional weakening of bonds to that center, and hence larger reductions in the frequencies of associated vibrational motions. The higher *A* factors for primary H-migration eliminations, then, are rationalized in terms of mass effects on the vibrational motions associated with the pentavalent silicon center (*i.e.*, X = CH_3 or SiH_3 is bound to the pentavalent silicon in the high *A* factor or primary H-migration reactions). If our transition state models are correct, still larger entropies of activation are predicted for reactants producing higher substituted pentavalent silicon centers in their transition states (*e.g.*, $(CH_3)_3SiSiH_3$).

The *A* factors for SiH_2: elimination from trisilane and methyldisilane differ by an amount consistent with their reaction path degeneracies (*i.e.*, reaction path degeneracy of reaction 2 = *R* ln 9; reaction path degeneracy (rpd) of reaction 6 = *R* ln 18; Δrpd ≃ 1.4 eu). Hence it is unlikely that these eliminations proceed *via* significantly different reaction paths. Thus, the decomposition of trisilane *via* a transition state involving a silicon bridge as pictured below in reaction 10 and as previously suggested[7] seems very unlikely since the corresponding transition state for the methyldisilane decomposition is excluded (*i.e.*, it would involve pentavalent carbon, and SiH_2 does not insert into either (C-Si) or (C-H) bonds in a competition with (Si-H) bonds).[3,4]



$$Si_3H_8 \longrightarrow H_3Si\overset{SiH_2}{\text{-----}}SiH_3 \longrightarrow Si_2H_6 + SiH_2 \qquad (10)$$

Heat of Formation of Methyldisilane. Reactions 2 and 6 can be combined by Hesse's law to obtain reaction 11: reaction 2 − reaction 6 = reaction 11. The Arrhenius parameters of the forward reactions 2 and 6 are reported in this study, and the relative rates of the back reactions (reactions −2 and −6) have been obtained in a prior study at 350°: $k_{-2}/k_{-6} = 0.20$.[7] Thus a value for the equilibrium constant of reaction 11 at 350° can be calculated: $K_{11} = (k_2/k_6)/(k_{-2}/k_{-6}) = 11.6$. Thermodynamic properties of disilane are known,[21] and the entropies, heat capacities, and heat contents of the other species of reaction 11 can be calculated from spectroscopic data using standard statistical thermodynamic methods[22] (see Table VI). Equation 12, then,

$$CH_3Si_2H_5 + Si_2H_6 \longrightarrow Si_3H_8 + CH_3SiH_3 \qquad (11)$$

$$\Delta H_{T(11)}° = T\Delta S_{T(11)}° - RT \ln K_{T(11)} \qquad (12)$$

can be employed to calculate the reaction enthalpy at 350°. With $K_{11} = 11.6$, $\Delta S_{11} = -0.31$ eu, one obtains $\Delta H_{11}° = -3.2$ kcal/mol. Correcting to 25° gives $\Delta H_{11}° = -2.8$ kcal/mol, and using the reported heats of formation for Si_2H_6, Si_3H_8, and CH_3SiH_3 ($\Delta H_f° = 17.1$,[23] 25.9[24] and

Table VI. Calculated Thermodynamic Properties of Methyldisilane[a] and Trisilane[b,c]

	T, °K				
	300	400	600	800	1000
		Methyldisilane			
$-(G_T° - H_0°/T$, cal/(deg mol)	67.11	70.59	79.49	86.45	92.77
$H_T° - H_0°$, kcal/mol	4.95	7.72	14.34	22.31	31.24
$S°$, cal/(deg mol)	81.60	88.69	101.62	112.82	122.61
C_P^0, cal/(deg mol)	25.38	29.88	37.30	42.58	46.48
		Trisilane			
$-(G_T° - H_0°)/T$, cal/(deg mol)	68.14	73.61	82.47	90.21	98.07
$H_T° - H_0°$, kcal/mol	5.46	8.50	15.84	24.39	31.50
$S°$, cal/(deg mol)	4.45	92.75	107.14	119.24	129.67
C_P^0, cal/(deg mol)	28.06	32.88	40.08	45.18	54.85

[a] Rotational barriers of 1.0 kcal/mol were used for $(SiH_3 \not\rightarrow X)$ rotors, and the methyl rotational barrier in methyldisilane was set at 1.7 kcal/mol as in methylsilane. [b] The following fundamental vibration frequencies were used in the calculations of the vibrational partition functions: for $CH_3Si_2H_5$ (cm^{-1})[c] 3 at (2940), 5 at (2150), 3 at (1330), 4 at (890), 1 ea at (1150), (820), (715), (700), (625), (420), (400), (380), (350), (185); for Si_3H_8 (cm^{-1})[c] 8 at (2150), 7 at (920), 2 at (625), 2 at (420), 2 at (380), 1 ea at (715), (400), (350), (135). [c] These assignments are based on our infrared spectra and assignments from CH_3SiH_3[28] and Si_2H_6.[29]

1.0[25] kcal/mol respectively), one obtains a value for the heat of formation of methyldisilane at 25°: $\Delta H_f°(CH_3Si_2H_5) = 12.6$ kcal/mol. Since a maximum error in K_{11} of 50% is estimated (corresponding to an error in $\Delta H_{11}°$ of only 0.5 kcal/mol) while entropies and enthalpy corrections contain negligible errors, this value for the heat of formation of $CH_3Si_2H_5$ is about as accurate as are the heats of formation used in its estimation.

Insertion Reactions. Thermochemistry and Kinetics. The *A* factors for silylene, silylsilylene, and methylsilylene insertion reactions (*i.e.*, reverse reactions −2, −6, −7, and −3, respectively) can be obtained from the observed *A* factors of the corresponding 1,2-H-shift eliminations, the reaction entropies of these processes at the mean reaction temperatures, and eq 13.

$$\log A(\text{atm}^{-1}\ \text{sec}^{-1})\ \text{insertion} = \log A(\text{sec}^{-1})\ 1,2\text{-H shift} + \frac{\Delta S°}{2.3R}\ (\text{insertion}) \quad (13)$$

The entropy of SiH_2: has been reported,[26] and the entropies of CH_3SiH and SiH_3SiH have been calculated by the difference method[27] starting from the known entropies of CH_3SiH_3 and Si_2H_6, respectively. Entropies used and *A* factors calculated are shown in Table VII. It is interesting to note that the *A* factors for SiH_2 insertions are close to collision frequencies, while the larger silylene insertions are only slightly slower (*i.e.*, they have steric factors of about 0.1). On entropy grounds, then, silylene insertion reactions are extremely efficient processes.

Since the rate constant ratio for silylene insertion into methylsilane and disilane is known (*i.e.*, at 350° $k_{-2}/k_{-6} = 0.20$), and the *A* factors for these processes calculated (Table VII), an estimate for the activation energy difference for SiH_2 insertion into methylsilane and disilane can be made. Thus from eq 14, one obtains $E_{-2} - E_{-6} = 1.1$ kcal/mol with an estimated error of the same magnitude.

$$(E_{-2} - E_{-6}) = RT(\ln k_{-6}/k_{-2} - \ln A_{-6}/A_{-2}) \quad (14)$$

While this activation energy difference is reasonable (predicting the higher activation energy for the insertion into the stronger Si–H bond), it is also of the same size as the experimental errors in the *A* factors and rate constants. The fact that E_{-2} and E_{-6} are different suggests that the activation energy for SiH_2 insertion into silicon–hydrogen bonds is not zero. Recently, John and Purnell have estimated the activation energy for SiH_2 insertion into SiH_4 to be 1.3 ± 1.1 kcal/mol.[28] Therefore, selecting a value of $E_{(\text{insertion})} \simeq 1.3 \pm 1.1$ kcal/mol, heats of formation of the silylenes formed in reactions 2, 3, 6, and 7 can be calculated. The values obtained, ignoring heat capacity corrections are: $\Delta H_f°(SiH_2:) = 61.1 \pm 1.1$ kcal/mol (from reaction 2) $= 60.6 \pm 1.1$ kcal/mol (from reaction 6); $\Delta H_f°(CH_3SiH:) = 53.1 \pm 1.1$ kcal/mol (from reaction 3); $\Delta H_f°(SiH_3SiH:) = 66.7 \pm 1.1$ kcal/mol (from reaction 7). Similarly, Purnell's results on the disilane decomposition give $\Delta H_f°(SiH_2:) = 57.9 \pm 1.1$ kcal/mol.

Table VII. *A* Factor and Relative Entropies of Silylene Insertion Reactions[a]

	Reaction −2 ($\bar{T} = 555°K$)		
	$SiH_2: +$	$CH_3SiH_3 \rightarrow$	$CH_3Si_2H_5$
$\bar{S}°$, (eu/mol)	55.1	73.6[b]	98.5
$\Delta S°_{-2} = -30.2$ eu; $A_{-2} = 10^{8.65}$ atm^{-1} sec^{-1} $= 10^{10.74}$ M^{-1} sec^{-1}			
	Reaction −3 ($\bar{T} = 555°K$)		
	$CH_3SiH: +$	$SiH_4 \rightarrow$	$CH_3Si_2H_5$
$\bar{S}°$, (eu/mol)	70.1	56.5	98.5
$\Delta S°_{-3} = -28.1$ eu; $A_{-3} = 10^{8.00}$ atm^{-1} sec^{-1} $- 10^{10.09}$ M^{-1} sec^{-1}			
	Reaction −6 ($\bar{T} = 545°K$)		
	$SiH_2: +$	$Si_2H_6 \rightarrow$	Si_3H_8
$\bar{S}°$, (eu/mol)	54.8	78.9[b]	102.9
$\Delta S°_{-6} = -30.8$ eu; $A_{-6} = 10^{8.94}$ atm^{-1} sec^{-1} $= 10^{11.02}$ M^{-1} sec^{-1}			
	Reaction −7 ($\bar{T} = 545°K$)		
	$SiH_3SiH: +$	$SiH_4 \rightarrow$	Si_3H_8
$\bar{S}°$, (eu/mol)	75.4	56.3	102.9
$\Delta S°_{-7} = -28.8$ eu; $A_{-7} = 10^{8.39}$ atm^{-1} sec^{-1} $= 10^{10.47}$ M^{-1} sec^{-1}			

[a] Entropy estimates in these reactions are easily accurate to within ±1.0 eu, corresponding to a factor of about 1.7 in Å. [b] Calculated from the standard entropy at 25°[21] and calculated heat capacities using reported vibrational frequencies.[29,30]

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References and Notes

(1) M. A. Ring, M. J. Puentes, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **92,** 4845 (1970). Also, recent results (to be published) on the pyrolysis of SiH_4 and Si_2H_6 with C_2H_2 strongly support silicon–hydrogen bond rupture as the initiation step in the silane pyrolysis system.
(2) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8,** 1787 (1969).
(3) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9,** 1068 (1970).
(4) M. Bowery and J. H. Purnell, *J. Amer. Chem. Soc.*, **92,** 2594 (1970).
(5) R. B. Baird, M. D. Sefcik, and M. A. Ring, *Inorg. Chem.,* **10,** 883 (1971).
(6) H. Sakuri, A. Hosemi, and M. Kumada, *Chem. Commun.*, 4 (1969).
(7) M. D. Sefcik and M. A. Ring, *J. Amer. Chem. Soc.*, **95,** 5166 (1973).
(8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N.Y., 1966, p 497.
(9) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, **5,** 549 (1966); *J. Amer. Chem. Soc.*, **90,** 3438 (1968).
(10) M. Scheisser and K. P. Ehlers, *Angew. Chem.*, **76,** 781 (1964); E. A. Chernyshev, N. G. Kamalenkov, and S. H. Bashkerova, *Zh. Obshch. Khim.,* **41,** 1175 (1971); R. L. Jenkins, A. J. Vanderwielen, S. P. Ruis, S. R. Gird, and M. A. Ring, *Inorg. Chem.*, **12,** 2968 (1973).
(11) M. Bowery and J. H. Purnell, *Proc. Roy. Soc., Ser. A.*, **321,** 341 (1971).
(12) C. S. G. Phillips and P. L. Timms, *Anal. Chem.*, **35,** 505 (1963).
(13) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93,** 6188 (1971).
(14) S. W. Benson, *Advan. Photochem.,* **2,** 1 (1964).
(15) W. B. Demore and S. W. Benson, *Advan. Photochem.*, **2,** 219 (1964).
(16) F. E. Saalfield and H. J. Svec, *Inorg. Chem.*, **3,** 1442 (1964); W. C. Steele and F. G. A. Stone, *J. Amer. Chem. Soc.*, **84,** 3599 (1962).
(17) R. P. Hollandsworth and M. A. Ring, *Inorg. Chem.*, **7,** 1635 (1968).
(18) Negative activation entropies might be expected for these reactions *a priori*, since H-bridge formation in the transition state necessarily restricts an internal rotation which contributes about 6.4 eu to the ground state entropy.
(19) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968, p 66.
(20) A. J. Vanderwielen, Ph.D. Thesis, San Diego State University, 1974.
(21) Reference 19, p 203.
(22) G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, "Thermodynamics," 2nd ed, McGraw-Hill, New York, N.Y., 1961, p 419.
(23) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65,** 779 (1961).
(24) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **68,** 946 (1964).
(25) P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, **74,** 719 (1970).
(26) P. John and J. H. Purnell, *J. Organometal. Chem.*, **29,** 233 (1971).
(27) H. E. O'Neal and S. W. Benson, *Int. J. Kinet.*, **1,** 221 (1969).
(28) P. John and J. H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, **69,** 1455 (1973).
(29) D. F. Ball, T. Carter, D. C. McKean, and L. A. Woodward, *Spectrochem. Acta*, **20,** 1721 (1964).
(30) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26,** 1107 (1957); H. S. Gutowsky and E. O. Stejskal, *J. Chem. Phys.*, **22,** 939 (1954).