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Shock-Induced Kinetics of the Disilane Decomposition and Silylene Reactions with Trimethylsilane and Butadiene

J. Dzarnoski, S. F. Rickborn, H. E. O'Neal,* and M. A. Ring*

Department of Chemistry, San Diego State University, San Diego, California 92182

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The homogeneous gas-phase decomposition kinetics of disilane have been studied by the comparative rate, single-pulse shock-tube technique in the 850–1000 K (2300–2700 torr) ranges. Two primary dissociation processes occur, $Si_2H_6 \xrightarrow{1} SiH_4 + SiH_2$ and $Si_2H_6 \xrightarrow{5} Si_2H_4 + H_2$, with Arrhenius parameters log k_1 (s^{-1}) = 14.36 − (48 810 ± 300 cal)/2.303RT and log k_5 (s^{-1}) = 15.3 − (55 300 ± 2200 cal)/2.303RT, respectively. In the presence of butadiene and trimethylsilane, silylenes produced in reaction 1 are efficiently trapped via reactions $SiH_2 + H_2C{=}CHHC{=}CH_2 \xrightarrow{9} H_2\overline{CHC{=}CHCH_2Si}H_2$ and $SiH_2 + Me_3SiH \xrightarrow{11} Me_3SiSiH_3$. The rate constants and activation energies of these reactions are roughly equal. At temperatures above 950 K, in the absence of trapping agents, hydrogen yields increase due to subsequent silylene dimerization, decomposition processes: $2SiH_2 \rightarrow Si_2H_4 \xrightarrow{10} Si_2H_2 + H_2$. The activation energy of the Si_2H_4 decomposition is estimated to fall within the range 51 800 < E_{10} < 56 000 cal.

Introduction

The homogeneous, gas-phase decomposition of disilane has been studied thoroughly by Bowrey and Purnell,[1] utilizing static system kinetic methods in the 283–340 °C (23–100 torr) ranges. A single primary process involving a 1,2-H shift between silicon centers (eq 1) was reported,

$$Si_2H_6 \xrightarrow{1} SiH_4 + SiH_2 \qquad (1)$$

with Arrhenius parameters of log A (s^{-1}) = 14.52 ± 0.36 and E = 49.24 ± 1.10 kcal/mol. The decomposition of trisilane[2] and of methyldisilanes[2-4] containing at least one hydridic hydrogen occur with very similar activation energies. By contrast, the dominant primary processes of monosilanes containing at least two hydridic hydrogens are three-center molecular hydrogen eliminations whose activation energies increase by 4–5 kcal/mol with each methyl substitution. Thus the primary decomposition modes of SiH_4,[5] $MeSiH_3$,[6] and Me_2SiH_2[6] (eq 2–4) have

$$SiH_4 \xrightarrow{2} SiH_2 + H_2 \qquad E_2 = 59.5\text{ kcal/mol} \qquad (2)$$

$$MeSiH_3 \xrightarrow{3} + H_2 \qquad E_3 = 63.2\text{ kcal/mol} \qquad (3)$$

$$Me_2SiH_2 \xrightarrow{4} Me_2Si + H_2 \qquad E_4 = 68.0\text{ kcal/mol} \qquad (4)$$

activation energies reported as shown. If electron-donating groups (like CH_3) raise the energy barrier to hydrogen elimination, then it is possible that electron-attracting groups (like SiH_3) will lower the energy barrier. Thus one might expect that the three-center hydrogen elimination from disilane (eq 5) could occur with an activation energy

$$Si_2H_6 \xrightarrow{5} SiH_3SiH + H_2 \qquad (5)$$

in the range of 56.5 ± 3 kcal/mol. The three-center hydrogen elimination reaction (5) could then be competitive with reaction 1 at higher temperatures.

In this paper we report on a study of the single-pulse, shock-induced decomposition of Si_2H_3 in the 850–1000 K (2500 ± 200 torr) range. The objectives of the study were to see if molecular hydrogen is produced in a primary decomposition mode like eq 5, to more firmly establish the Arrhenius parameters of the silane formation reaction by extending the experimental temperature range of study some 400 °C, and to study subsequent reactions of the silylene primary process products under homogeneous reaction conditions.

Table I. Yield Data for the Disilane Decomposition in "Excess" Toluene[a]

% decompn	T, K	$\Delta(SiD_4)/\Delta(Si_2D_6)$	$\Delta(D_2)/\Delta(Si_2D_6)$
13.7	913	0.7999	0.2147
13.8	913	0.8019	0.1899
15.5	918	0.8152	0.2190
16.5	921	0.7439	0.2237
29.2	947	0.8851	0.1997
29.4	948	0.7823	0.2279
37.9	961	0.8065	0.1997
38.3	962	0.7779	0.2125
39.9	964	0.7441	0.2013
51.7	980	0.7194	0.2306
53.8	982	0.7948	0.2267
67.0	999	0.8470	0.2297
73.3	1007	0.7721	0.2732
85.9	1026	0.7910	0.3730
93.0	1041	0.7409	0.4664
96.5	1053	0.7539	0.5670
97.4	1057	0.6811	0.5483

[a] $[toluene]_0/[Si_2D_6]_0$ = 10/1.

Mechanism of Decomposition

Two reactant mixtures were shocked and reacted at temperatures ranging from 830 to 1005 K: mixture 1 (0.2% Si_2D_6, 3.0% $PhCH_3$ in argon); mixture 2 (0.5% Si_2D_6, 5.0% butadiene in argon). Products of mixture 1 were SiD_4, D_2, and trace amounts of HD. Reactant mixture 2 produced these same products and also the butadiene trapping product for SiD_2, namely, 1,1-dideuteriosilacyclopent-3-ene. Yield data, displayed as (mol of product/mol of Si_2D_6 reacted) vs. % Si_2D_6 decomposed, are shown in Tables I and II. Note that for both reactant mixtures, SiD_4 and D_2 yields were quite constant over a wide range of disilane decompositions. Thus for mixture 1 (i.e., in excess toluene), with decompositions ranging from 14 to 67%, $\Delta(SiD_4)/\Delta Si_2D_6)$ = 0.79 ± 0.06 and $\Delta(D_2)/\Delta(Si_2D_6)$ = 0.21 ± 0.03; and for mixture 2 (i.e., in excess butadiene), with decompositions ranging from 12 to 89%, $\Delta(SiD_4/\Delta(Si_2D_6)$ = 0.83 ± 0.06 and $\Delta(D_2)/\Delta(Si_2D_6)$ = 0.15 ± 0.04. Note also

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[5] C. G. Newman, H. E. O'Neal, M. A. Ring, F. Leska, and N. Shipley, *Int. J. Chem. Kinet.*, **11**, 1167 (1979).

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Table II. Yield Data for the Disilane Decomposition in Ten Times 1,3-Butadiene

% reactn	T, K	$\Delta(SiD_4)/\Delta(Si_2D_6)$	$\Delta(D_2)/\Delta(Si_2D_6)$	$\Delta(\text{adduct})^a/\Delta(Si_2D_6)$
11.9	907	0.8325	0.1742	0.6019
15.1	917	0.8375	0.1457	0.5782
43.2	968	0.8113	0.1560	0.4603
43.9	969	0.8755	0.1456	0.3897
49.6	977	0.7891	0.1606	0.5153
60.8	991	0.7891	0.1455	0.4528
71.3	1004	0.8173	0.1120	0.4899
71.4	1004	0.8679	0.1768	0.4716
79.8	1016	0.8393	0.1319	0.5918
85.8	1025	0.7602	0.2015	0.5715
88.4	1030	0.8186	0.2063	0.5841
89.7	1033	0.7443	0.2187	0.6453
91.9	1038	0.7589	0.2781	0.5809

[a] The quantities of the adduct are *not* absolute values and only demonstrate change as a function of percent decomposition.

that the sums of the siilane and hydrogen yields are unity within experimental error. The simplest explanation of these observations, and the one we favor, is that SiD_4 and D_2 arise from separate and distinct primary processes (eq 6 and 7). If so, the rate constant ratios for these processes

$$Si_2D_6 \xrightarrow{6} SiD_4 + SiD_3 \tag{6}$$

$$Si_2D_6 \xrightarrow{7} Si_2D_4 + D_2 \tag{7}$$

are the same within experimental error over the temperature range of study: $k_6/k_7 \simeq 4.26 \pm 1.0$ between 850 and 1005 K.

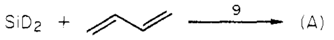
This analysis assumes that the SiD_4 and D_2 products arise exclusively from eq 6 and 7. This seems reasonable since, while secondary reactions of the free radicals SiD_3 and D with disilane would also produce silane and hydrogen, there are no reasonable homogeneous gas-phase formation reactions for these radicals at shock temperatures. Further, if such species were involved, significant yields of HD would be expected in the presence of toluene. Only trace yields of HD were observed.

An alternative explanation of our data is that eq 6 is the only primary process and that the deuterium yields arise from the subsequent decomposition of silane (eq 8). This

$$SiD_4 + (M) \xrightarrow{8} SiD_2 + (M) + D_2 \tag{8}$$

possibility, however, must be excluded in our studies on the basis of the known stability of silane.[5] Thus from the rate constant for SiH_4 formation at our highest temperature ($k_1(1005\text{ K}) = 4070\text{ s}^{-1}$) and the rate constant for silane decomposition at that temperature ($k_8(1005\text{ K}) \simeq 83\text{ s}^{-1}$),[5] one can calculate by relations for consecutive first-order reactions that less than 1.8% of the silane formed in eq 6 will subsequently decompose during a representative shock period of 350 μs. Further, if SiD_4 decomposition were the source of D_2, the hydrogen yields would not be constant with increasing T (as observed) but rather would increase strongly with increasing temperature. We conclude, therefore, that the observations are best explained in terms of two competitive primary processes dissociation reactions (eq 6 and 7).

At high conversions of Si_2D_6 in the presence of toluene (i.e., mixture 1 at temperature $\geq$1000 K), the yields of D_2 do increase and they increase significantly. While subsequent decomposition of SiD_4 may be a contributing factor to these increasing D_2 yields, the major factor is almost certainly due to decomposition of silylene dimers $(SiD_2)_2$. Thus in our shock-tube kinetic studies on SiH_4 at temperatures above 1170 K, the values of $\Delta(H_2)/\Delta(SiH_4)$ were 1.85 ± 0.10.[5] This demonstrates almost quantitative decomposition of SiD_2 via its dimer. One would therefore expect yields of D_2 to increase with temperature in the disilane decomposition at temperatures above 1000 K. Apparently this reaction channel is not significant at temperatures below 950 K. That SiD_2 via its dimer is the source of the "extra" D_2 at high temperatures is also supported by our observations that butadiene suppresses the extra D_2 formation yields. Thus butadiene is known to be an efficient chemical trap for silylene (eq 9).



(9)

Although absolute yields of the silacyclopentene were not obtained, the relative ratio $\Delta(A)/\Delta(Si_2D_6)$ was constant at a function of Si_2D_6 decomposition, hence efficient trapping of SiD_2 via rxn 9 is suggested.

If the hydrogen yields of the disilane and silane shock-induced decompositions are in part due to subsequent silylene dimer decompositions (eq 10), as suggested here,

$$Si_2H_4 + (M) \xrightarrow{10} HSiSiH + H_2 + M \tag{10}$$

then upper and lower limits can be placed on the activation energy of this process. Thus, the constancy of H_2 yields in the disilane decomposition at temperatures below 990 K requires that the lifetime of the Si_2H_4 dimer be long relative to the reaction residence time (e.g., $^{\tau}(Si_2H_4)$ ($T <$ 990 K) $> 3^{\tau}(\text{residence}) \simeq 900\ \mu\text{s}$). A reasonable estimate of the A factor for the decomposition (i.e., $A_{10} \simeq 10^{14.5}\text{ s}^{-1}$) then establishes that $E_{10} \geq 51\,800$ cal. Similarly, the high hydrogen yields of the silane decomposition at $T > 1170$ K requires that $^{\tau}(Si_2H_4)$ ($T < 1170$ K) $< {}^1/_3\,{}^{\tau}(\text{residence}) \simeq 100\ \mu\text{s}$. This requires that $E_{10} < 56\,000$ cal.

Decomposition Kinetics of Disilane

Kinetic data for the disilane decomposition are given in Table III. The comparative rate internal standard was *tert*-butyl chloride which decomposes quantatively to isobutene and HCl according to the kinetics, log k (t-BuCl, s^{-1}) = 13.9 − 46 200 cal/θ.[7] First-order rate constants for disilane were based on the amount of disilane reacted, and first-order rate constants for *tert*-butyl chloride were based on the amounts of isobutene formed. Reaction temperatures are those calculated from the observed rate constants for the *tert*-butyl chloride and its decomposition Arrhenius parameters.

Reaction 1. SiH_4 Formation. Since disilane is in its pressure fall-off regime under our experimental conditions (850–1000 K (2300–2700 torr)), RRKM calculations[8] were made relative to the silane formation reaction. The fall-off corrections, $k/k(\infty)$, are shown in column 4 of Table III. These are based on the Bowrey and Purnell kinetic results ($A_1 = 10^{14.52}\text{ s}^{-1}$; $k_1(585\text{ K}) = 1.33 \times 10^{-3}\text{ s}^{-1}$) and on collision efficiencies calculated from an equation suggested by Troe[11-13] ($\beta_c = (1 + (T/x)_2)^{-1}$ with $x = 350$ for argon and

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(7) W. Tsang, *J. Chem. Phys.*, **40**, 1498 (1964).

(8) RRKM calculation procedure: input k(exptl) at T and P (total) collision efficiencies, reactant and transition-state frequencies, and a guessed $k(\text{uni})/k(\infty)$. An iterrative technique calculates $k(\text{uni})/k(\infty)$ to 1% accuracy, from which $\Delta E^{\circ}{}_0{}^{*}$ and E_a(exptl) are obtained. Then the k(uni) vs. P at various temperatures are calculated in the usual manner.[9] State densities and state sums are calculated by using the Beyer–Swinehart alogorithm.[10]

(9) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York (1972).

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(11) A. Croce and J. Troe, International Symposium, "Berthelot-Vieille-Mallard-Le Chatelier", First Specialists Meeting (International), Combustion Institute, University de Bordeaux I, July 20–24, 1981.

Table III. Kinetic Data for the Decomposition of Disilane and *tert*-Butyl Chloride

T, K	ln $k(Si_2H_6)^c$	ln $k(C_4H_8)$	$k_1/k(\infty)^a$	ln $k_1(\infty)^b$
834.3	3.6214	4.1373	0.90	3.516
855.3	4.6785	4.8229	0.88	4.596
859.6	4.7031	4.9576	0.88	4.620
861.2	4.9247	5.0090	0.87	4.853
862.1	4.6025	5.0378	0.87	4.531
863.9	4.9910	5.0933	0.87	4.920
867.4	4.9919	5.2000	0.86	4.932
869.6	4.7230	5.2686	0.85	4.675
871.9	5.1110	5.3404	0.85	5.063
876.3	5.4142	5.4734	0.85	5.366
894.5	5.8008	6.0129	0.83	5.776
916.3	6.2883	6.6323	0.81	6.288
916.7	6.1179	6.6413	0.81	6.118
917.3	6.2378	6.6596	0.81	6.238
920.0	6.3485	6.7336	0.80	6.361
920.9	6.4614	6.7590	0.80	6.474
924.2	6.5638	6.8491	0.79	6.589
931.7	6.2985	7.0517	0.79	6.324
933.6	6.6296	7.1024	0.78	6.667
944.9	6.7431	7.4002	0.77	6.794
951.0	7.1676	7.5585	0.76	7.231
951.8	7.1134	7.5777	0.76	7.177
957.6	7.1621	7.7248	0.75	7.239
964.1	7.5971	7.8895	0.74	7.688
985.8	7.9926	8.4202	0.73	8.097
986.9	7.7069	8.4466	0.73	7.811
988.4	7.9966	8.4820	0.72	8.114
995.2	8.0953	8.6423	0.70	8.620
1005.2	8.4744	8.8746	0.70	8.620

[a] RRKM fall-off correction. [b] See ref 15. [c] ln $k(Si_2H_6) = \ln(k_1 + k_5)$.

x = 1100 for toluene). An Arrhenius plot of the experimental rate constants (column 2, Table III) gives log $(k_1 + k_5) = 12.92 - (42796 \pm 3130)/2.303RT$ which may be compared to the RRKM-predicted parameters for eq 1 under the shock-tube conditions of log $k_1(\text{RRKM}) = 14.10 - 47610$ cal/$2.303RT$. The experimental parameters are clearly too low,[14] which may be indicative of some mechanistic complications, but also could in part be caused by uncertainties in RRKM collision efficiences (β_c).

The Arrhenius parameters of the calculated high-pressure rate constants (column 5, Table III) are log $k_1(\infty, s^{-1}) = 13.51 - (45248 \pm 3250$ cal$)/2.3RT$ which are lower than the Bowrey and Purnell values but in agreement within the experimental errors of the two studies. An extended Arrhenius plot of the high pressure rate constants from both shock-tube and static system studies is shown in Figure 1, and it is apparent that the studies are in good agreement.

The Arrhenius plot now covers an enormous temperature range (i.e., 550–1005 K), and the composite Arrhenius parameters derived from all the data reflect the expected reduction in experimental error. Thus with average rate constant errors in the static and shock-tube systems of 6.6% and 7.1%, respectively, one calculates log $k_1(\infty, s^{-1}) = 14.36 \pm 0.09 - (48810 \pm 300$ cal$)/2.303RT$.

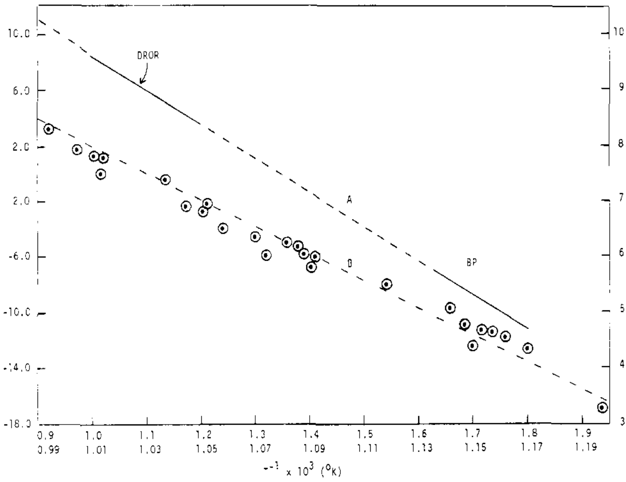

Figure 1. Arrhenius plots of rate constants for $Si_2H_6 \xrightarrow{1} SiH_4 + H_2$: (a) line A, combined Arrhenius plot of Bowrey and Purnell (BP) static system results and the data of this study (DROR); (b) line B, Arrhenius plot of $k_1(\infty)$ values of this study; (c) dotted lines correspond to extrapolations of the BP Arrhenius line.

Reaction 5. H_2 Formation. For the static system study of the disilane decomposition (556–613 K), Bowrey and Purnell reported reaction 1 as the only primary dissociation process even though hydrogen was a reaction product. These authors identified hydrogen as a secondary reaction product on the basis of the behaviors of the hydrogen formation curves in time. The latter were linear within experimental errors up to 5% disilane reaction, and they extrapolated to zero product yield at *finite* reaction times. While this appears to be good evidence for the secondary product role of hydrogen, it should be noted that at conversions above 5%, the rates of hydrogen production were pronounced and they increased markedly in time. Thus, small curvatures in the H_2 curves at shorter reaction times are expected. These could very easily produce the "observed" finite time intercept behaviors. Initial hydrogen yields, then, could in fact be measures of the primary dissociation reaction 5. With this assumption, the data of Bowrey and Purnell can be used to obtain a measure of the relative rates of the two primary process rate constants, namely $k_1/k_5 = 32.8 \pm 22$ at 585 K. This same ratio, from our data, has a value of $k_1/k_5 = 4.26 \pm 1.0$ at mean shock temperatures of 925 K. Thus one can calculate that $E_5 - E_1 = 6.5 \pm 2.2$ kcal/mol and $A_5/A_1 = 8.06$. Thus log $A_5 = 15.26$ and $E_5 \simeq 55.3 \pm 2.2$ kcal/mol. These are *minimum* values since some of the hydrogen product at 585 K could well have arisen from wall-induced reactions at proposed by Bowry and Purnell. Nevertheless, this activation energy compares very favorably with the value of $E_5 \simeq 55.0$ kcal/mol obtained using our observed rate constant for reaction 5 at 925 K scaled to the high-pressure limit ($k_5(\infty) = 0.19k(\text{exptl})\ (k(\infty)/k(\text{exptl})) = 180\ s^{-1}$), and an estimated A factor for the reaction obtained by analogy with the CH_3SiH_3[6] decomposition A factor adjusted for reaction path degeneracy (i.e., $A_5 = 2 \times 10^{14.95}\ s^{-1} = 10^{15.25}\ s^{-1}$). We therefore believe that there are two primary dissociation processes in the disilane decomposition and that their kinetics can be fairly accurately described by

$$\log k_1\ (s^{-1}) = 14.36 - (48810 \pm 300\ \text{cal})/2.303RT$$

$$\log k_5\ (s^{-1}) = 15.3 - (55300 \pm 2200\ \text{cal})/2.303RT$$

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(12) The values for x suggested by Troe were x = 150 for inert gases, x = 300 for reactants, and x = 600 for large molecules. These values, however, do not give as satisfactory agreement with the observed falloff in the cyclopropane isomerization in shock tube studies as do the X values utilized here. Further, the β_c values used here appear to be more consistent with calculated β's derived from data on a number of low-pressure unimolecular reaction systems (see ref 13).

(13) J. Troe, *J. Chem. Phys.*, **66**, 4758 (1977); H. Endo, K. Glonzer, and J. Troe, *J. Phys. Chem.*, **83**, 2083 (1979); J. Troe, *ibid.*, **83**, 114 (1979).

(14) While the Arrhenius parameters seem significantly different, one finds that the experimental rate constants are in fact quite close to those predicted by the RRKM calculations. Thus at the lowest temperature (834 K), k(exptl) is 21% larger than calculated, while at the highest temperature (1005 K), k(exptl) is 26% smaller than calculated.

(15) The high-pressure rate constants for reaction 1 were obtained from the relation $k(\infty) = (k(\text{exptl})\ 0.81\ (k(\infty)/k(\text{exptl})))$, where 0.81 is the primary process yield of reaction 1 in the disilane decomposition under shock conditions and $k(\infty)/k(\text{exptl})$ are the RRKM fall-off parameters for reaction 1.

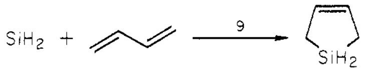
Table IV. Product Ratio (A/B) from SiH_2 Reaction with $H_2C{=}CHHC{=}CH_2$ and Me_3SiH[a]

% Si_2H_6 decompn	T, K	ratio (A/B) obsd	ratio (A/B) calcd
28.2	946	1.20	0.73
29.0	947	1.34	0.86
31.2	951	1.47	0.84
50.6	978	1.64	0.52
60.7	991	1.94	0.40
61.6	992	1.89	0.38
69.8	1002	2.31	0.29
83.9	1022	5.19	0.18
87.4	1028	9.30	0.21

[a] A = $H_2CHC{=}CHCH_2SiH_2$; B = $H_3SiSi(Me)_3$.

Relative Rates of Reactions of Silylene with Trimethylsilane and Butadiene

The rates of silylene insertion into the Si–H bond of Me_3SiH relative to its rates of addition to 1,3-butadiene (eq 9 and 11) were studied at temperatures between 930 and 1015 K.



A (9)

$$SiH_2 + Me_3SiH \xrightarrow{11} \underset{B}{Me_3SiSiH_3} \qquad (11)$$

In these studies, silylene was generated from the shock initiated decomposition of disilane in the presence of excess trimethylsilane and butadiene ($Me_3SiH/H_2C{=}CHHC{=}CH_2/Si_2H_6 = 10/10/1$). The results are presented in Table IV. Observed product yield ratios (Table IV, column 3) are those calculated from the GLPC peak areas of the trapped products (B and A) corrected for their relative sensitivities. (The FID detector is primarily sensitive to the organic portion of a molecule. Thus, relative sensitivities for A and B should be very similar to those for butadiene and Me_3SiH.) Because silacyclopentene is thermally stable at formation temperatures while the 1,1,1-trimethyldisilane product is quite unstable, the observed yield ratios represent maximum values for the rate constant ratio k_9/k_{11}. The calculated yield ratios (column 4, Table IV) were obtained by calculating the concentration of Me_3SiSiH_3 that would have been needed at time zero to produce the observed yields of Me_3SiSiH_3 at the end of the shock periods. These hypothetical initial concentrations divided by product A yields produce overestimates of the true yields, hence the calculated yield ratios represent *minimum* values for the k_9/k_{11} ratio. The calculations utilized the known Arrhenius parameters for the Me_3SiSiH_3 decomposition:[4] $\log k_{-11} = 14.45 - 48000$ cal/$2.303RT$. The true k_9/k_{11} ratio, then, must fall somewhere between these two extremes. At low conversions the observed and calculated k_9/k_{11} value should converge, and the data in Table IV show this to be the case. From Table IV, one can estimate that at 930 K, $k_9/k_{11} = 1.0 \pm 0.3$.

There are lower temperature data which pertain to this same rate constant ratio. Thus the relative rate of silylene insertion into Si_2H_6 vs. addition to butadiene was measured at 658 K,[16] while the relative rate of silylene insertion into Si_2H_6 vs. insertion into Me_3SiH has been measured at 623° K.[17] Ignoring the slight temperature difference between these studies, one can calculate from the reported data a rate constant ratio for the reactions of interest of $k_9/k_{11} = 0.89 \pm 0.3$ (623–658 K). The ratio k_9/k_{11}, therefore, appears to be essentially constant over a 300 K temperature range, and the difference in the activation energies for silylene addition to butadiene and insertion into the Si–H bond of trimethylsilane is very small (i.e., $E_9 - E_{11} = 475 \pm 2300$ cal/mol). Similar results have been observed for the relative rates of SiH_2 addition to butadiene vs. insertion into SiH_4 where an activation energy difference of 2.6 kcal/mol has been observed.[18]

Experimental Section

The single-pulse shock tube used in this study was similar to that described by Jeffers and Shaub[19] and has been previously described by us.[5] Arrival times of the shock waves were monitored by a Kistler Model 211 B-3 pressure transducer, along with a Kistler 549 piezotron coupler, a Tektronix 545A Oscilloscope, and a C-12 camera system. The composition of the reaction mixtures were (a) Si_2D_6 (0.2%), toluene (3%), Xe (0.2%), and Ar (96.5%), (b) Si_2D_6 (0.5%), $H_2C{=}CHHC{=}CH_2$ (5%), Xe (.5%), and Ar (94%), (c) Si_2H_6 (1.1%), *tert*-butyl chloride (0.4%), Xe (1.1%), and toluene (2.8%), Ar (94.6%), and (d) Si_2H_6 (0.2%), Me_3SiH (2.0%), $H_2C{=}CHHC{=}CH_2$ (2.0%), Xe (0.2%), and Ar (95.6%). Reaction times measured at the end plate were on the order of 350 μs while reaction pressures were on the order of 2500 mmHg.

Silicon hydride and hydrogen analyses were carried out on a Hitachi Perkin-Elmer RMU-6E mass spectrometer with Xe used as the inert internal standard. Relative sensitivities were obtained from standard reactant and product mixtures. The 1,1,1-trimethyldisilane and 1-silacyclopent-3-ene were identified mass spectrometrically and by GLPC retention times compared with authentic samples. GLPC analyses were carried out with a Varian 1400 (and 1200) aerograph gas chromatograph employing either Paropak Q or SF96 columns.

The disilane decomposition was followed mass spectrometrically using xenon (m/e 131) as an internal standard and m/e 68 as a measure of the disilane loss. The rate constants were calculated from the relation

$$k_{DS} = 1/\tau \ln (Si_2H_6/Xe)_0/(Si_2H_6/Xe)_t$$

The *tert*-butyl chloride decomposition was monitored by gas chromatographic analysis for *tert*-butyl chloride (*t*-BuCl) and 1,1-dimethylethylene (*i*-Bu). The *t*-BuCl decomposition rate constants were calculated from the relation

$$k(t\text{-BuCl}) = \frac{1}{\tau} \ln \left[\frac{t\text{-BuCl} + \text{wf}(i\text{-Bu})}{t\text{-BuCl}} \right]$$

where wf = area ratio (*t*-BuCl/*i*-Bu)/mole ratio (*t*-BuCl/*i*-Bu)] and *t*-BuCl and *i*-Bu are the GLPC product peak areas.

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Registry No. B(pz)$_4$Rh(dq), 82323-69-1; B(pz)$_4$Rh(cod), 81420-85-1; B(pz)$_4$Rh(nbd), 82323-70-4; butadiene, 106-99-0.

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