

Decomposition Kinetics of 1,1,2,2-Tetramethyldisilane and of 1,1-Dimethyldisilane

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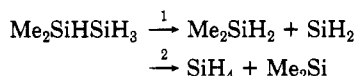
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The thermal decomposition kinetics of the titled compounds were studied in the presence of butadiene in order to isolate the kinetics of their primary dissociation reactions. Arrhenius parameters for the single reaction channel of tetramethyldisilane (eliminating Me_2Si to form Me_2SiH_2) were $\log A_5 = 13.17 \pm 0.24$ and $E_5 = 47.42 \pm 0.64$ kcal; Arrhenius parameters for the two primary dissociation channels of dimethyldisilane (reaction 1 eliminating SiH_2 to form Me_2SiH_2 and reaction 2 eliminating Me_2Si to form SiH_4) were $\log A_1 = 15.50 \pm 0.21$ and $E_1 =$ and 50.99 ± 0.59 kcal and $\log A_2 = 13.18 \pm 0.28$ and $E_2 = 51.79 \pm 0.77$ kcal. From these and other results it is confirmed that A factors for silylene elimination reactions from polysilanes depend strongly on the nature of the eliminated silylene: for SiH_2 and other totally hydrogenated silylenes (e.g., SiH_3SiH), $A = 10^{15.4 \pm 0.4} \text{ s}^{-1}$; for MeSiH and methylated silylsilylenes (e.g., Me_2SiHSiH), $A = 10^{14.4 \pm 0.4} \text{ s}^{-1}$; for Me_2Si and other doubly alkylated silylenes, $A = 10^{13.4 \pm 0.4} \text{ s}^{-1}$.

Introduction

The thermal decomposition kinetics of disilane and various methylated disilanes have recently been the focus of attention because of their importance to heat of formation estimates of SiH_2 , MeSiH , and Me_2Si . Thus disilanes containing an Si-H bond are known to decompose by 1,2-H shifts to produce a monosilane and silylene product (e.g., reactions 1 and 2). Disilane decomposition

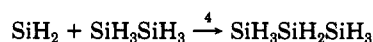
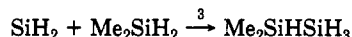


kinetics, coupled with reaction entropies and back reaction rate constants, provide decomposition reaction enthalpies from which silylene heats of formation can be calculated (assuming known heats of formation for the other reaction species). Clearly, the accuracy of silylene heats of formation obtained in this fashion depends on the accuracy of the decomposition reaction Arrhenius parameters and also on the validity of the identification of those parameters with the initial 1,2-H shift processes. Early kinetic data on disilane decompositions (e.g., data for the decompositions of disilane,¹ methyldisilane,² 1,1,2-trimethyldisilane,³ and pentamethyldisilane³) were obtained from low conversion data for systems without added silylene trapping agents. It is now known that silylene chain reactions occur in the decomposition of alkylsilanes (RSiH_3 , $\text{R} > \text{CH}_3$)⁴ and similar chain reactions are expected to occur in the disilane systems. Therefore identification of the early experimental Arrhenius parameters with 1,2-H shift reaction parameters has been questioned.⁵ Arrhenius parameters for decompositions generating Me_2Si (A factors in the $10^{13.0 \pm 0.4} \text{ s}^{-1}$ range) seemed particularly suspect when compared to the considerably higher A factors of decompositions generating SiH_2 ($A \approx 10^{15.4 \pm 0.4} \text{ s}^{-1}$). Investigations and reinvestigations of methylated disilane decomposition kinetics under maximum inhibition of silylene chains, therefore, seemed desirable. To this end, both Walsh⁶ and Davidson⁷ have restudied the pentamethyldisilane thermal

decomposition under inhibition, and we report here first time investigations of the inhibited decomposition kinetics of 1,1-dimethyldisilane (DMDS) and of 1,1,2,2-tetramethyldisilane (TMDS).

Experimental Section

Normal and dideuterated 1,1,2,2-tetramethyldisilane were prepared by reduction of the 1,2-dichloro-1,1,2,2-tetramethyldisilane with either LiAlH_4 or LiAlD_4 . The dichloride reactant was obtained from the reaction of $\text{Me}_2\text{SiPhSiPhMe}_2$, commercially available from Petrarch, with HCl over AlCl_3 as described by Kumada et al.⁸ Dimethyldisilane was obtained by flow pyrolysis of a 200 Torr, 20% Si_2H_6 in Me_2SiH_2 gaseous mixture through a 16-mm diameter \times 23 cm tubular oven maintained at 625 K. Residence times corresponding to about 50% decomposition of the disilane (i.e., ≈ 6 min) were used. The dimethyldisilane and trisilane products formed by the silylene insertion reactions 3 and 4 were condensed in a liquid N_2 bath and separated by trap distillation.



The trisilane was then removed by reaction with LiH in a monoglyme slurry at room temperature⁹ (producing SiH_4 and polymer). Even though DMDS alone is not reactive toward LiH , about 50% of the DMDS product was also lost in this process. Overall DMDS yields (based on disilane reacted) were about 15% of theoretical. Both DMDS and TMDS reactants, identified by infrared and MS analyses, were purified by standard trap to trap vacuum line distillations and were found to be better than 99.6% pure by GC analyses. In particular, no contamination by the main reaction products or by trisilane could be detected (i.e., contaminant concentrations relative to the reactants were less than 4×10^{-5}).

The decompositions of TMDS and DMDS were studied extensively by static methods. Reaction mixtures contained reactant in roughly 1/1 ratios with internal GC standards (tetramethyldisilane for TMDS; propane for DMDS), varying amounts of silylene chain inhibitor, and (in the case of TMDS) about 90% argon diluent. Butadiene was the main silylene chain inhibitor for both studies. Inhibition ratios (In.R.) employed were as follows: $[\text{trap}]/[\text{reactant}] = \text{In.R.} = 10/1, 30/1, \text{ and } 60/1$ in the TMDS studies and $20/1, 40/1, \text{ and } 80/1$ in the DMDS studies. TMDS was also studied by using trimethylsilane in an In.R. of 30/1 and (less completely) by the single pulse shock tube comparative rate

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Table I. Kinetic Results for the Thermal Decomposition of 1,1,2,2-Tetramethyldisilane

trap	In.R. ^a	T range, K	log A ^b	E, ^b kcal	(10 ⁴ k) ₆₁₅	
A. Static System Results						
C ₄ H ₆	10/1	580–651	12.94 ± 0.55	46.55 ± 1.50	2.49	b
C ₄ H ₆	30/1	585–650	13.29 ± 0.40	47.76 ± 1.11	2.07	b
C ₄ H ₆	60/1	573–650	13.12 ± 0.28	47.28 ± 0.78	2.08	b
C ₄ H ₆	both	573–650	13.17 ± 0.24	47.42 ± 0.64	2.07	c
Me ₃ SiH	30/1	591–648	13.38 ± 0.66	48.17 ± 1.86	1.73	d
B. Shock-Tube, Comparative Rate Results						
C ₄ H ₆	30/1	1107–1142	14.46 ± 1.99	55.13 ± 10.28		d
C ₄ H ₆	30/1	615–1125	12.71 ± 0.20	46.14 ± 0.80		e

^aIn.R. = inhibition ratio = [trap]/[reactant]. ^bErrors shown correspond to ±2σ. Arrhenius parameters are based on dimethylsilane formation. ^cArrhenius parameters of the combined rate constants of the 30/1 and 60/1 butadiene inhibited mixtures. ^dSee text concerning analysis reproducibilities in these systems. ^eArrhenius parameters based on the rate constants at the mean temperatures of the static and shock-tube studies with errors estimated on the basis of 10% errors in the rate constants at static system temperatures and 30% errors in the rate constants at shock-tube temperatures.

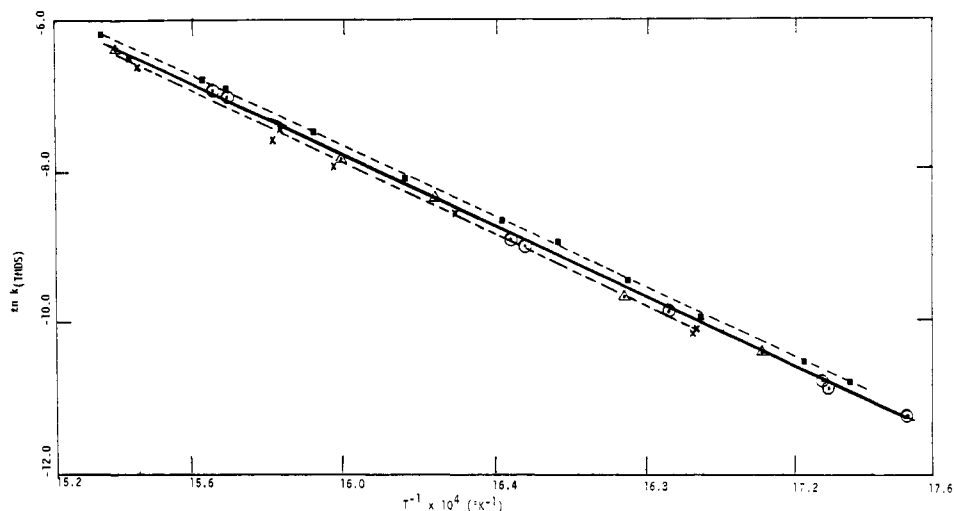


Figure 1. Arrhenius plots of the decomposition rate constants of 1,1,2,2-Tetramethyldisilane at various levels of inhibition: \square (---), 10/1 C₄H₆/TMDS; \triangle (—), 30/1 C₄H₆/TMDS; \circ (—), 60/1 C₄H₆/TMDS; \times (---), 30/1 Me₃SiH/TMDS.

technique^{10,11} with 1/1 cyclopropane as the internal kinetic standard, 30/1 butadiene, and 97% argon diluent. Total pressures used in the kinetic runs ranged from 50 to 200 Torr, and the temperature ranges investigated were 573–650 K for TMDS and 573–623 K for DMDS.

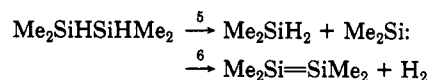
The products observed from the TMDS decompositions in the presence of inhibitors were dimethylsilane and the expected trapping products (pentamethyldisilane in Me₃SiH and 1,1-dimethylsilacyclopent-3-ene in C₄H₆). Methane and hexamethyltrisilane were also observed in the TMDS neat pyrolysis. The products observed in the DMDS decompositions were dimethylsilane and silane. The trapping products of SiH₂ and Me₂Si with butadiene were certainly also formed but not observed possibly due to "hang-up" on the GC column.

Product analyses in the TMDS system were made with a Varian 3700 FID gas chromatograph coupled to an HP-3390A integrator using either a Supelco SPB-1 wide bore capillary column or a Supelco SE-30 packed column. The capillary column gave excellent product separations but was not reproducible in the analysis of heavy species (e.g., the TMDS reactant and the Me₂Si with trimethylsilane and butadiene trapping products). Consequently, when capillary column GC analyses were used, reaction rates were calculated from product formation data. Analyses for most of the 60/1 butadiene static system runs were made by using the SE-30 GC column. Heavy mass species analyzed consistently on this column and reasonably good mass balances (within the analysis errors) were realized. Thus (DMS)_{formation}/(TMDS)_{loss} = 1.00 ± 0.07, for conversions exceeding 10%. D₂ analyses in the shock-induced decomposition of D₂-TMDS were made with an AEI 902 mass spectrometer.

Analyses of the reactant and products (SiH₄ and Me₂SiH₂) of the dimethylsilane decomposition were made on a Varian 1400 thermal conductivity GC using a stainless-steel 4 ft × 1/8 in. Poropak N column programmed between 80 and 110 °C. GC detection by thermal conductivity was necessary because flame analysis of silane is insensitive and nonreproducible. The DMDS pyrolysis was studied over conversions ranging from 30 to 85%. Such large conversions were required because of the very small amounts of silane produced in the minor primary dissociation reaction channel. Mass balances were excellent: (SiH₄ + DMS)_{formation}/(DMDS)_{loss} = 1.00 ± 0.02.

Results and Discussion

Tetramethyldisilane. TMDS has only one primary dissociation channel (reaction 5). The 1,2-H₂ elimination (reaction 6), thought to be a possible dissociation channel



by analogy with the disilane decomposition,¹² does not occur. This was demonstrated by the absence of D₂ in the products of the shock-induced decomposition of 1,2-di-deuterated TMDS. This negative observation is consistent with a recently calculated barrier of 86 kcal for the analogous 1,2-H₂ elimination from Si₂H₆.¹³

Table I shows the Arrhenius parameters obtained from least-squares analyses of TMDS decomposition rate con-

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Table II. Kinetic Results for the Thermal Decomposition of 1,1-Dimethyldisilane
A. Static System Results

In.R. ^a	log A ₁₊₂ ^e	E ₁₊₂ ^e	log A ([DMS]/[S]) ^e	(E _S - E _{DMS}) ^e	k ₁₊₂₍₆₀₀₎ ^f
20.1 ^b	15.21 ± 0.41	50.14 ± 1.1	2.015 ± 0.48	0.815 ± 1.327	8.81
80/1 ^c	15.41 ± 0.04	50.72 ± 0.10	2.210 ± 0.18	0.834 ± 0.494	8.58
40/1 ^d	14.48	48.14	[DMS]/[S] _{594K} = 231 [DMS]/[S] _{616K} = 248		8.78
In.R.	log A ₁	E ₁ , kcal	log A ₂	E ₂ , kcal	
∞/1	15.50 ± 0.21	50.99 ± 0.59	13.18 ± 0.28	51.79 ± 0.77	

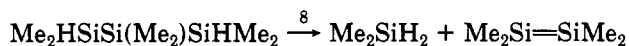
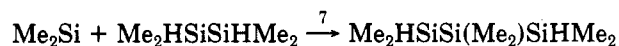
B. Eq I Results

$$\text{intercept} = k_1/k_2 = 10^{2.31 \pm 0.06} e^{+0.812 \pm 0.12/RT}$$

$$\text{slope} = k_{\text{eff}}/k_{\text{BD}} = 10^{-1.04 \pm 1.00} e^{-0.770 \pm 2.74/RT}$$

^aIn.R. = inhibition ratio = [C₄H₆]/[TMDS]. ^bTemperature range was 568–616 K; three temperatures. ^cTemperature range was 578–626 K; five temperatures. ^dOnly two temperatures investigated; 616 K was common to all studies. ^eArrhenius parameters of the yield ratios (Y(S)/Y(DMS)). Errors shown are statistical and correspond to ±2σ. Real errors are larger; units of A and k are s⁻¹; units of E are kcal. ^fOverall rate constants (s⁻¹) for DMDS decomposition at 600 K.

stants based on dimethylsilane formation under various degrees of inhibition. Figure 1 shows Arrhenius plots of the data. Decompositions were studied at eleven temperatures for the 10/1 inhibited systems, five temperatures for the 30/1 inhibited systems, and eight temperatures for the 60/1 system. Conversions ranged from 7 to 56%. Since the mean temperature (T_m ≈ 615 K) rate constants and Arrhenius parameters of the 30/1 and 60/1 mixtures were found to be the same within experimental error, their combined parameters (k_{TMDS} = 10^{13.17 ± 0.24} e^{-47 424 ± 642 cal/RT} s⁻¹) can be identified with the initial step of the decomposition (i.e., reaction 5). The lower parameters and higher rate constants at T_m of the 10/1 C₄H₆/TMDS reaction mixture indicates some silylene-induced reactant decomposition at this inhibition level. The products supply no information on the reactions responsible for the induced decomposition (since our observations found them to be invariant with the level of inhibition); however, the reaction 7 and 8 sequence proposed previously to explain the neat dimethylsilane pyrolysis system¹⁴ seems a likely possibility.



Slightly higher Arrhenius parameters and slightly lower rate constants were found for the TMDS decomposition under trimethylsilane inhibition. Usually this would be interpreted as evidence for nonmaximum inhibition in systems with added butadiene. However, Me₃SiH inhibition rate data were complicated by reactant analytical problems (already mentioned), and methane was found to be an important product: [CH₄]/[Me₂SiH₂] yield ratios varied from 0.16 to 0.46 and appeared to decrease with increasing amounts of conversion. While the methane source is not known, there is some evidence to suggest that it arises via catalytic decomposition of TMDS on the walls. Thus rapid TMDS loss and significant methane production was observed when TMDS at low pressures (≈0.03–0.30 Torr in argon) was reacted at 599 K. At this temperature the apparent first-order rate constants for CH₄ formation were comparable to homogeneous first-order rate constants for dimethylsilane production (i.e., k_{methane} ≈ 4.5 × 10⁻⁵ s⁻¹ compared to k_{DMS} = 7.3 × 10⁻⁵ s⁻¹). Also, TMDS loss rates were much higher (k_{TMDS,loss} ≈ 1.4 × 10⁻³ s⁻¹). By contrast, at 50 Torr TMDS (i.e., a TMDS pressure more than an order of magnitude higher than that of the butadiene inhibited studies) no methane was formed and the rate constants for TMDS loss (k_{TMDS} ≈ 8 × 10⁻⁵ s⁻¹) were only slightly higher than those calculated for the homogeneous

reaction (as might be expected). These observations indicate a zero-order surface reaction of TMDS, quenchable by butadiene but not by trimethylsilane, producing mainly reactant loss but also some CH₄. It is interesting to note that no evidence for this kind of wall catalysis was found by Davidson³ in his pentamethyldisilane study at reactant pressures between 1 and 7 Torr. Assuming similar catalytic susceptibilities for tetra- and pentamethyldisilane, this is curious and can only be rationalized on the basis of quite different wall coatings in the two experimental systems. We conditioned our reactor walls by pyrolyzing silane or disilane to produce "inert" silicon mirror surfaces. This procedure may have inadvertently caused catalysis (rather than preventing it) as there are now reports of specific silicon-induced heterogeneous effects in the pyrolyses of silicon hydrides larger than disilane.¹⁵

The TMDS decomposition at an In.R. = 30 was studied under shock tube conditions with cyclopropane as the internal standard. Unfortunately analytical problems for reactant persisted through these studies. In addition, cyclopropane was a poor choice of kinetic standard as it decomposed an order of magnitude slower than the reactant at reaction temperatures. Also, rate constants of both reactions had to be corrected for falloff. Consequently, decomposition rate constants (based on DMS formation) were not very accurate (see the Arrhenius parameters of Table I). Nevertheless, because of the large temperature range, a fairly reliable measure of the reaction 5 activation energy is apparently realized by a combined Arrhenius treatment of the static and shock tube studies: E₅ ≈ 46.1 ± 0.8 kcal, in agreement with the preferred static system value (E₅ = 47.4 ± 0.6 kcal) within the errors.

The TMDS A factor under butadiene inhibition can be identified with the 1,2-H shift Me₂Si elimination from TMDS: A_{TMDS} = 10^{13.17} s⁻¹. This is very similar to other recently reported A factors for Me₂Si elimination reactions,^{6,7,16} and it is consistent with thermochemical estimates.¹⁷ Thus the entropy loss from restricted rotation around the Si–Si bond in the "tight" transition state is about 3.5 eu, and with a reaction path degeneracy (rpd) of 2, A_{est} ≈ 10^{13.0} s⁻¹.

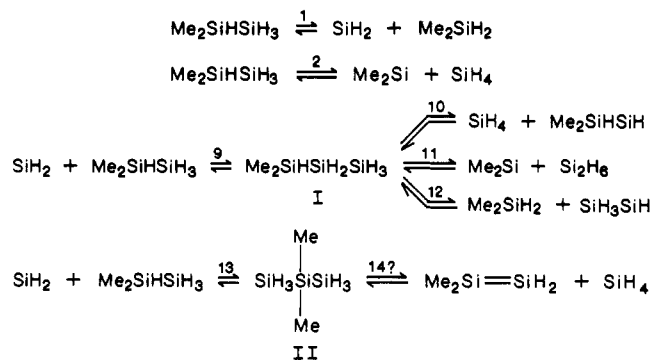
1,1-Dimethyldisilane. Two primary dissociation reaction channels (reactions 1 and 2) are possible in the thermal decomposition of DMDS. For this reason the possibility of silylene-induced decomposition of DMDS (e.g., via reactions 9–14) is high.

However, under butadiene inhibition, silylene-induced chain decomposition of the reactant is not significant.

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Thus for the three levels of butadiene inhibition studied, overall reaction rate constants at $T_m \approx 600$ K and overall reaction Arrhenius parameters were the same within the errors (see Table II). By contrast, the strong dependency of the ratios of the product yields of the main reaction products (dimethylsilane/silane = DMS/S; see Table II) shows that *complete* quenching of the primary product silylenes was not realized in these studies. In the absence of propagation reactions (e.g., reactions 9 and 14), or under conditions of complete inhibition, the DMS/S ratios should be direct measures of the primary dissociation channels (reactions 1 and 2); they should also be constant at any given temperature. In fact, the DMS/S ratios increased from about 200 (for the 20/1 inhibited reactions) to about 300/1 (for the 80/1 inhibited reactions). Clearly SiH_2 elimination (reaction 1) is by far the dominant dissociation channel, and the possibility that it is the *only* primary dissociation channel needs to be considered.

Assuming that reaction 1 is the only important source of dimethylsilane and that silane can be produced in a primary dissociation reaction (reaction 2) as well as from reactions subsequent to reactions 9 and 13, one can derive by steady-state methods the Stern-Volmer type relationship of eq I. Here, k_{eff} is the effective rate constant for $\text{Y}(\text{SiH}_4)/\text{Y}(\text{Me}_2\text{SiH}_2) =$

$$k_2/k_1 + (k_{\text{eff}}/k_{\text{BD}})([\text{DMDS}]/[\text{C}_4\text{H}_6]) \quad (\text{I})$$

silane production from reactions subsequent to 9 and 13, and k_{BD} is the rate constant for silylene trapping by butadiene. Arrhenius fits of the DMS/S product yield data for the 20/1 and 80/1 $\text{C}_4\text{H}_6/\text{DMDS}$ reactant mixtures gave $\text{Y}(\text{DMS})/\text{Y}(\text{S}) = 10^{2.02}e^{815\text{cal}/RT}$ and $\text{Y}(\text{DMS})/\text{Y}(\text{S}) = 10^{2.21}e^{834\text{cal}/RT}$, respectively. Plots of these data according to eq I gave the following slopes and intercepts (in Arrhenius form): slope = $10^{-1.04 \pm 1.00}e^{-766 \pm 2740\text{cal}/RT}$; intercept = $10^{2.31 \pm 0.04}e^{812 \pm 120\text{cal}/RT}$.¹⁸ The nonzero intercepts show that Me_2Si elimination from DMDS did compete with SiH_2 elimination in our studies. Coupling the intercepts (whose errors were surprisingly low) with the experimental DMDS loss kinetics (best represented by results of the 80/1 inhibition studies, $k_{\text{DMDS}} = 10^{15.41 \pm 0.04}e^{-(50.72 \pm 0.10)/RT}$ s⁻¹) yields Arrhenius parameters for the two dissociation channels: $\log A_1 = 15.50 \pm 0.21$, $E_1 = 50.99 \pm 0.59$ kcal, $\log A_2 = 13.18 \pm 0.28$, and $E_2 = 51.42 \pm 0.77$, (A factors in s⁻¹, E 's in kcal). The most significant finding here is that Me_2Si elimination has an A factor more than 2 orders of magnitude lower than SiH_2 elimination (in agreement with Davidson's⁷ observations and with A factors observed for Me_2Si eliminations from TMDS¹⁶ and pentamethyldisilane^{6,7}). In addition, the activation energy for Me_2Si elimination is very comparable to (but perhaps slightly higher than) that of the SiH_2 elimination. Finally, it is interesting to note

that the relative rates of the primary dissociation reaction channels at decomposition temperatures are very nearly in the same ratio as their reverse insertion reactions^{5,19} at room temperature, i.e., $(k_1/k_2)_{600} \approx 400$ and $(k_{-1}/k_{-2})_{300} \approx 550$. With the reasonable assumption of negligible temperature effects for the latter ratio, this indicates equal or very similar enthalpies for the two competing silylene elimination reactions (reactions 1 and 2); consequently H replacement by Me at a silicon center of a silane or polysilane has the same stabilizing effect as it does at a silylene center.

Equation I slope interpretation is equally interesting although more ambiguous because of the rather sizable errors. The reaction of SiH_2 with reactant can proceed by reactions 9–14, and two of these produce silane. Steady-state treatment of these reactions yields $k_{9,\text{eff}} = k_9k_{10}/[(k_{-9} + k_{10} + k_{11} + k_{12}) + k_{13}k_{14}/(k_{-13} + k_{14})]$. Ignoring the second term of the denominator (since there is no evidence yet for this type of elimination and it is expected to be the smaller term in any case) and knowing that SiH_2 and SiH_3SiH eliminations should dominate, $k_{\text{eff}} \approx k_9k_{10}/(k_{-9} + k_{12})$. Slopes, then, measure the product of competition between SiH_2 trapping by reactant vs butadiene (k_9/k_{BD}) and the competition between the decompositions of the trisilane (I) to silane vs other products ($k_{10}/(k_{-9} + k_{12})$). Observations of relative SiH_2 trapping by Si_2H_6 and C_4H_6 at disilane pyrolysis temperatures²⁰ suggest that the former (k_9/k_{BD}) can be assigned a value near unity. Therefore at reaction temperatures, $k_{10}/(k_{-9} + k_{12}) \approx 5 \times 10^{-2}$. New results on the trisilane decomposition kinetics²⁰ show A factors for SiH_2 and SiH_3SiH eliminations of $10^{15.66}$ and $10^{15.34}$, respectively, and by analogy one might expect similar A factors for corresponding reactions of (I), i.e., $A_9 \approx A_{12} \approx 10^{15.4 \pm 0.4}$ s⁻¹. It is also reasonable to assume similar activation energies for the three competing processes reactions –9, 10, and 12). Therefore, the A factor for Me_2SiHSiH elimination should be in the range of $A_{10} \approx 10^{14.4 \pm 0.04}$ s⁻¹. This value is comparable to A factors found for MeSiH eliminations from disilanes.⁷

Summary

The implications of the present results and those of trisilane relative to the nature of the transition states involved are as follows: silylene eliminations and Si–H insertion reactions involving fully hydrogenated species (e.g., SiH_2 , SiH_3SiH) occur through very loose transition states with elimination A factors in the $10^{15.4 \pm 0.4}$ s⁻¹ range; increased alkylation at the α -Si center (as in MeSiH and Me_2Si) or even alkylation at the β -Si center (as in Me_2SiHSiH) results in transition state tightening and progressively lower elimination A factors with increasing methylation (e.g., $10^{14.4 \pm 0.4}$ s⁻¹ for MeSiH and $10^{13.4 \pm 0.4}$ s⁻¹ for Me_2Si); and replacements of an H at a silylene center by Me_2SiH or Me groups produce silylenes of similar reactivities.

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Registry No. TMDS, 814-98-2; TMDS- d_2 , 53490-52-1; DMDS, 16342-86-2; C_4H_6 , 106-99-0; Si_2H_6 , 1590-87-0; Me_2SiH_2 , 1111-74-6; Me_2Si , 6376-86-9; 1,2-dichloro-1,1,2,2-tetramethyldisilane, 4342-61-4.

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(18) These results are consistent with data from all three In.R. studies at their only common temperature, 616 K.