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Mechanism of the Thermal Decomposition of Dimethylsilane at Atmospheric Pressures in the Gas Phase

H. E. O'Neal* and M. A. Ring*

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

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A mechanism for the gas-phase, high-pressure thermal decomposition of dimethylsilane is proposed which explains in a kinetically reasonable way the production of the complex linear and cyclic carbosilane products observed for this reaction. The mechanism is based on unimolecular and bimolecular reactions of silylenes, which (with one exception) are all well-known or previously proposed processes. A crude modeling of the dimethylsilane pyrolysis, using assigned rate constants derived from reported Arrhenius parameters (or by analogy with reported parameters) or from thermochemical kinetic considerations in the absence of such data, is shown to be in reasonable agreement with the experimental data.

Introduction

A comprehensive mechanistic interpretation of the origins of the numerous and unusual products observed and characterized by Fritz et al.[1] in their classic studies of the pyrolyses of methylsilanes ($\text{Me}_n\text{SiH}_{4-n}$, $n = 1$–4) has never been made. Initially, and perhaps still today, these pyrolyses were thought to involve mainly free radical reactions.[2] However, with progress in characterizations of the initiation reactions in the methylsilane pyrolyses[3-7] and with a reasonably good understanding of the subsequent elementary reactions involved,[5,6] it is now clear that silylenes (and silenes and disilenes) and not free radicals must be the main reaction intermediates of these pyrolyses. Hence a logical explanation of their reaction products on this basis should now be possible. Such is the purpose of this paper. In particular, we present here a reasonable mechanistic interpretation of the dimethylsilane pyrolysis.

The following facts concerning alkylsilane and alkyldisilane pyrolyses are now rather well documented: (1) Primary dissociation reactions for all alkylmonosilanes (except tri- and tetraalkylmonosilanes) produce silylenes or their silene isomers.[7] For example, the most important primary process reactions of dimethylsilane are reactions I and II.

$$\text{Me}_2\text{SiH}_2 \xrightarrow{\text{I}} \text{Me}_2\text{Si} + \text{H}_2 \qquad \phi = 0.71$$

$$\text{Me}_2\text{SiH}_2 \xrightarrow{\text{II}} \text{MeSiH} + \text{CH}_4 \qquad \phi = 0.15$$

Free radical production by reaction III is negligible at $t < 1000$ K but can be an important primary process at higher temperatures.

$$\text{Me}_2\text{SiH}_2 \xrightarrow{\text{III}} \text{Me}^\bullet + \text{Me}\dot{\text{S}}\text{iH}_2$$

(2) Primary dissociation reactions of disilanes and alkyldisilanes (except hexaalkyls) also produce silylenes. Thus methyldisilane decomposes initially by reactions IV and V.[8]

$$\text{MeSiH}_2\text{SiH}_3 \xrightarrow{\text{IV}} \text{MeSiH}_3 + \text{SiH}_2$$

$$\text{MeSiH}_2\text{SiH}_3 \xrightarrow{\text{V}} \text{MeSiH} + \text{SiH}_4$$

Three-center 1,1-H_2 elimination (as in reaction VI) is a generally accepted reaction pathway in disilanes.[9]

$$\text{MeSiH}_2\text{SiH}_3 \xrightarrow{\text{VI}} \text{MeSiH}_2\text{SiH} + \text{H}_2 \qquad \text{1,1-H}_2 \text{ elimination}$$

Four-center 1,2-H_2 elimination from disilanes is crucial to our subsequent mechanistic treatment, and a thorough discussion of how this type of process can be effected is given later.

Silylenes are known to be the dominant reaction intermediates in alkylsilane pyrolyses and much is now known

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Table I

reaction type	reactions	log A^a	E, kcal	ref
	Silylene Insertions into Si–H Bonds			
a	$Me_2\ddot{Si} + Me_2SiH_2 \xrightarrow{2} Me_2SiHSiHMe_2$	9.5	0 ± 2	32
	Disilane Decompositions			
b	$Me_2SiHSiHMe_2 \xrightarrow{3} Me_2SiH_2 + Me_2\ddot{Si}$	12.9	48 ± 2	25
c + d	$\xrightarrow{4} Me_2Si{=}SiMe_2 + H_2$ (multistep, see text)			
	Silylene ⇄ Disilene Isomerizations			
e	$Me_2Si{=}SiMe_2 \xrightarrow{5} Me_3Si\ddot{Si}Me$	13.0	40 ± 5	16
f	$MeHSi{=}SiMe_2 \xrightarrow{63} Me\ddot{Si}SiHMe_2$	13.5	17 ± 5	16
g	$Me_3SiSi(Me){=}SiMe_2 \xrightarrow{64} Me\ddot{Si}SiMe_2SiMe_3$	13.0	14 ± 4	17
	Silylene ⇄ Silene Isomerizations			
h	$Me_2\ddot{Si} \xrightarrow{65} CH_2{=}SiHMe$	13.0	40 ± 4	18
	Intramolecular Silylene Insertions (into C–H Bonds)^b			
i	$Me_3Si\ddot{Si}Me \xrightarrow{8} \underbrace{Me_2Si{-}SiHMe}_{CH_2}$	13.0	34 ± 4	19
j	$Me_3SiCH_2\ddot{Si}Me \xrightarrow{14} \underbrace{Me_2SiCH_2SiHMe}_{CH_2}$	12.0	30 ± 4	19
k	$Me_3SiCH_2SiH_2CH_2\ddot{Si}Me \xrightarrow{48} \underbrace{Me_2SiCH_2SiH_2CH_2SiHMe}_{CH_2}$	10.5	24 ± 4	19
	Disilacyclopropane Ring-Opening Reactions			
l	$\underbrace{Me_2Si{-}SiMeH}_{CH_2} \xrightarrow{10} Me_2HSiCH_2\ddot{Si}Me$	13.7	10 ± 4	16
m	$\underbrace{Me_2Si{-}SiMeH}_{CH_2} \xrightarrow{12} Me_3SiCH_2\ddot{Si}H$	12.5	26 ± 4	16
n	$\underbrace{Me_2Si{-}SiMeH}_{CH_2} \xrightarrow{66} Me_2Si{=}CH_2 + Me\ddot{Si}H$	14.5	41 ± 5	20
	Addition Reactions of Silylenes and Silenes			
o	$Me_2\ddot{Si} + Me_2\ddot{Si} \xrightarrow{67} Me_2Si{=}SiMe_2$	7.7	0	20
p	$Me_2\ddot{Si} + CH_2{=}SiMeH \xrightarrow{67} \underbrace{Me_2Si{-}SiMeH}_{CH_2}$	7.4	0	20
q	$CH_2{=}SiMeH + CH_2{=}SiMeH \xrightarrow{68} \underbrace{MeHSiCH_2SiHMe}_{CH_2}$	6.6	0	21

^{a}Errors in A are estimated to be about a factor of $10^{\pm 0.5}$. ^{b}The same reactions for RSiH (rather than RSiMe, as above) have lower activation energies by about 4 kcal.

about the reaction possibilities of these species. For example, silylenes can initiate and propogate chain reactions (via Si–H insertion reactions when such reactions produce assymetric disilanes),[7] they can decompose to olefins and smaller silylenes[7] (i.e. for silylenes of formula RSiH when R > CH_3), and they can isomerize via intramolecular C–H insertion reactions to produce a variety of cyclic products.[10] The latter intramolecular insertions can be three-center to form silacyclopropanes (which are unstable to subsequent decompositions and isomerizations even at room temperature),[11] four-center to produce silacyclobutanes (which are relatively stable up to quite high temperatures),[12] five-center to form silacyclopentanes (also thermally stable),[13] and six-center to form silacyclohexanes (the most stable of the cyclic products).[13] The three-center processes are believed to be the most facile;[14] however under certain conditions higher center intramolecular insertions can be competitive.[15]

Reactions Operative in the Dimethylsilane Pyrolysis

Based on the above, it is possible to identify specific reaction types that should reasonably be central to the dimethylsilane pyrolysis. These are illustrated in Table I along with their approximate Arrhenius parameters either

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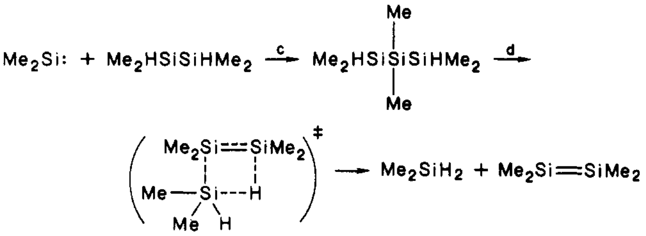
obtained from the literature (reactions a, b, h, and q) or estimated by using thermochemical kinetic methods[23] from literature data as cited. [Units are s^{-1} or $M^{-1}\ s^{-1}$; reaction *types* are indicated by lower case letters and specific reactions are numbered to correspond to the modeling (see Table V).

Effective 1,2-H_2 Elimination from Disilanes

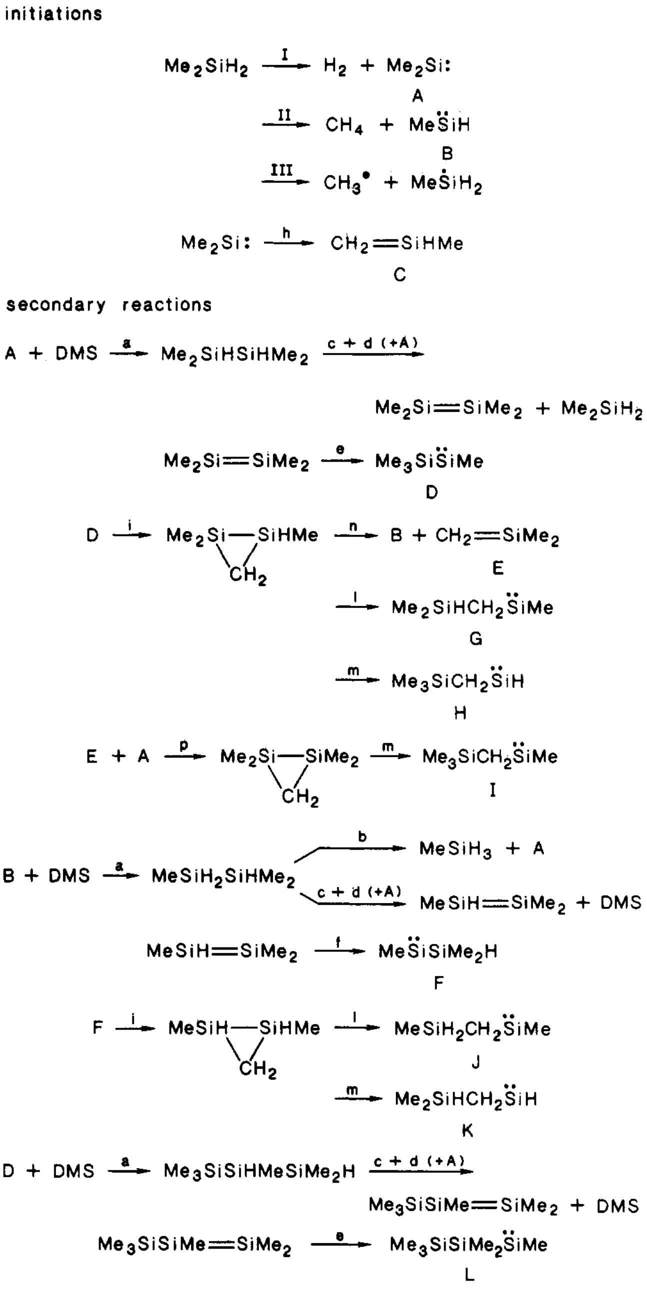
Conversions of disilanes to their disilenes are extremely important to our mechanism for the dimethylsilane pyrolysis. While single-step, four-center hydrogen eliminations do not occur in disilane pyrolyses (theoretical calculations of the energy surface for four-center hydrogen elimination gives an energy barrier of 86 kcal;[24] also, no hydrogen is produced in the shock-initiated decompositon of 1,1,2,2-tetramethyldisilane[25]), there is an attractive reaction sequence (reaction c + d, shown below) which leads to the same end result. Four-center elimination in organodisilanes with OMe rather than H bridging has recently been reported by Jones et al.[26] Also, four-center eliminations of HX (X = Cl, Br, I, OH, SH, OMe, etc.) are very common unimolecular processes in organic compound decompositions.[27] Therefore, the c + d reaction sequence seems reasonable and our modeling was done on this basis.



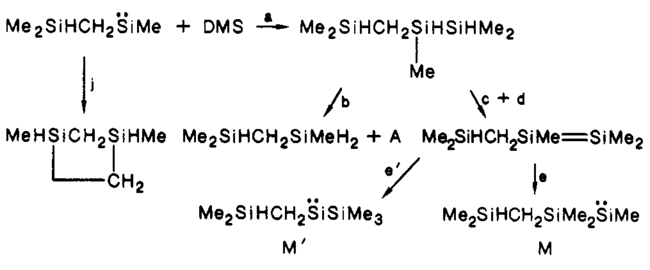
Conditions and Observations on the Dimethylsilane Pyrolysis

The pyrolysis of dimethylsilane[1,2] was carried out under continuous flow conditions. An approximate initial 200-Torr pressure of dimethylsilane was maintained by passing the circulating gases over the liquid reactant held in a −45 °C reservoir. The 1-m long plug flow reactor was thermostated at temperatures in the 600 °C range. Product yield data reported for the pyrolysis are reproduced in Scheme VI. From this scheme we see that 42% of the products were linear carbosilanes [1,3-disilapropanes (39%) and 1,3,5-trisilapentanes (3%)], while 22% of the products were cyclic carbosilanes [1,3-disilacyclobutanes (4%), 1,3,5-trisilacyclohexanes (12%), and 1,3,5-tetrasilaadamantanes (6%)].

Scheme I. Initiation Reactions and the Generation of Primary (A–F) and Secondary (G–L) Reaction Intermediates in the Dimethylsilane (DMS) Pyrolysis



Scheme II. Secondary Reaction Intermediate Reactions Illustrated for Species G[a]



[a] e′ is and e-type isomerization to an internal silylene.

Mechanism of the Dimethylsilane Pyrolysis

A thermochemically and kinetically reasonable mechanistic interpretation for the pyrolysis of dimethylsilane, based on the reaction possibilities presented earlier, is given in Scheme I–III. Scheme I shows the initiation reactions of the dimethylsilane pyrolysis and the reactions which generate primary (A–F) and secondary (G–L) reaction intermediates. Scheme II shows reactions of intermediate G that are typical of the secondary intermediates. Isolatable products and higher molecular weight tertiary intermediates produced in the Scheme II reactions of all secondary intermediates (G–K) are summarized in Table II. Scheme III shows the reactions of tertiary intermediate M, and Table III shows the products expected

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Table II. Formations of 1,3-Disilapropanes, 1,3-Disilacyclobutanes, and Intermediate Precursors to the Larger Carbosilanes: Reactions of Intermediates G–K[a]

reactants	reaction paths	products, new intermediates	no. of Si–H bonds
G + DMS	a, b	A + $Me_2SiHCH_2SiH_2Me$	3
	a, c + d, e	H_2 + $Me_2SiHCH_2SiMe_2\ddot{Si}Me$ (M)	1
	a, c + d, e′	H_2 + $Me_2SiHCH_2\ddot{Si}SiMe_3$ (M′)	
	k	$MeSiHCH_2SiHMeCH_2$	2
H + DMS	a, b	A + $Me_3SiCH_2SiH_3$	3
	a, c + d, e	H_2 + $Me_3SiCH_2SiMeH\ddot{Si}Me$ (N)	1
	a, c + d, e′	H_2 + $Me_3SiCH_2\ddot{Si}SiMe_2H$ (N′)	1
	k	$Me_2SiCH_2SiH_2CH_2$	2
I + DMS	a, b	A + $Me_3SiCH_2SiH_2Me$	2
	a, c + d, e	H_2 + $Me_3SiCH_2SiMe_2\ddot{Si}Me$ (O)	0
	a, c + d, e′	H_2 + $Me_3SiCH_2\ddot{Si}SiMe_3$ (O′)	0
	k	$Me_2SiCH_2SiHMeCH_2$	1
J + DMS	a, b	A + $MeSiH_2CH_2SiH_2Me$	4
	a, c + d, e	H_2 + $MeSiH_2CH_2SiMe_2\ddot{Si}Me$ (P)	2
	a, c + d, e′	H_2 + $MeSiH_2CH_2\ddot{Si}SiMe_3$ (P′)	2
	k	$SiH_2CH_2SiHMeCH_2$	3
K + DMS	a, b	A + $Me_2SiHCH_2SiH_3$	4
	a, c + d, e	H_2 + $Me_2SiHCH_2SiHMe\ddot{Si}Me$ (Q)	4
	a, c + d, e′	H_2 + $Me_2SiHCH_2\ddot{Si}SiMe_2H$ (Q′)	2
	k	$MeSiHCH_2SiH_2CH_2$	3

[a] G = $Me_2SiHCH_2\ddot{Si}Me$; H = $Me_3SiCH_2\ddot{Si}H$; I = $Me_3SiCH_2\ddot{Si}Me$; J = $MeSiH_2CH_2\ddot{Si}Me$; K = $Me_2SiHCH_2\ddot{Si}H$.

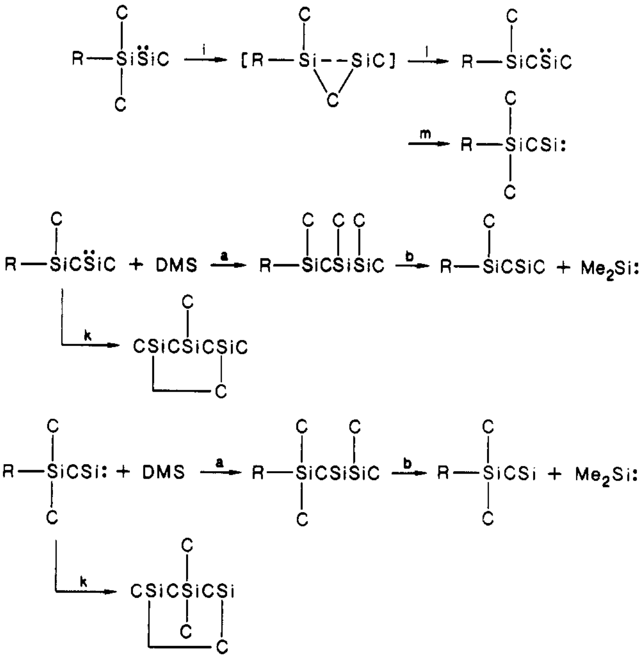
for all the tertiary intermediates (M–Q′).

Secondary reaction intermediates (G–L) can react in at least three ways: (1) with DMS to produce 1,3 disilapropanes (reactions a and b), (2) with DMS and then with dimethylsilylene (A) to produce silylsilylenes of structures $\equiv SiCSi\ddot{Si}$— (reactions a, c + d, and e), and (3) by intramolecular C—H insertions (reaction j) to produce 1,3-disilacyclobutanes. These reactions are shown in Scheme II. [In subsequent tables and discussions a shorthand notation is used to represent reaction species. Hydrogens are not shown, and silylene centers are indicated by dots. Thus dimethylsilylene is $C\ddot{Si}C$ and 1,1,2,2-tetramethyldisilane is C_2SiSiC_2.]

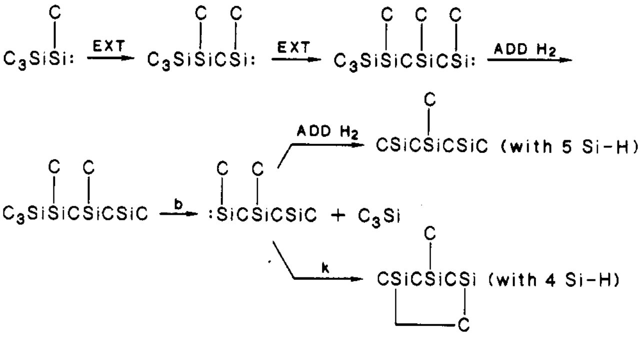
Tertiary intermediates M through Q′ are responsible for higher molecular weight carbosilane products. On rearrangements to carbosilane structures (via reactions of type i, l, and m), the resultant silylenes hydrogenate (reactions a and b) to produce linear 1,3,5-trisilapentane products or undergo six-center intramolecular C–H insertions (reactions of type k) to produce 1,3,5-trisilacyclohexane products. Still higher molecular weight silylenes can also be generated. The former two reaction pathways are illustrated in Scheme III for species (M).

Note again that silylene reactions with DMS have three different end results: (1) hydrogenation of the silylene center, reaction sequence a and b (henceforth indicated as H_2 ADD) [this sequence constitutes a silylene-induced chain decomposition of the reactant since A is regenerated], (2) extension of the carbosilane backbone of the silylene by one Me_2Si unit, reaction sequence a, c + d, e, i, and then l or m (henceforth indicated by EXT), e.g., R(C)Si: $\xrightarrow{EXT}$ R(C)$_2$SiCSi: or R(C)SiC$\ddot{Si}$C, and (3) conversion of a methyl (or H) group bonded to a silylene center into a trimethylsilyl (or dimethylsilyl) group with retention of the silylene center, reaction sequence a, c + d, and e′ (henceforth indicated by BLOCK), e.g., R(C)Si: $\xrightarrow{BLOCK}$ R$\ddot{Si}$SiC$_3$. The BLOCK substitution has important consequences as it provides reasonable explanations for adamantane product formations and also for trisila product distributions as functions of their Si–H bond contents. Thus experimentally, the favored products of the tertiary intermediates are the trisilapentanes and trisilacyclohexanes with five Si–H and four Si–H bonds, respectively. According to Table III, however, intermediates G and H (which should be most important as they arise from the reactions of A and D) produce products with one less H. This apparent contradiction can be explained by following the consequences of DMS trapping of D via EXT and ADD sequences as shown in Scheme IV.

Scheme III. Tertiary Intermediate Reactions to Products (Illustrated for Species M; M = RSiMe$_2\ddot{Si}$Me and R = Me$_2$SiHCH$_2$–)

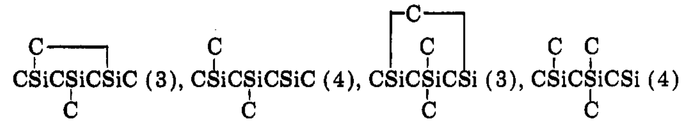
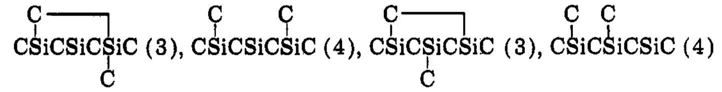
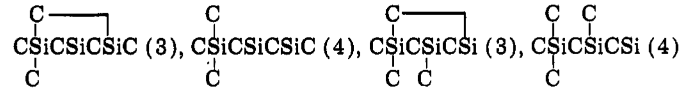
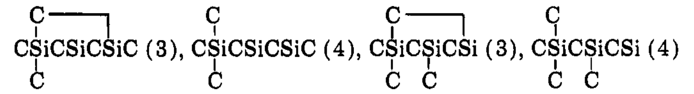
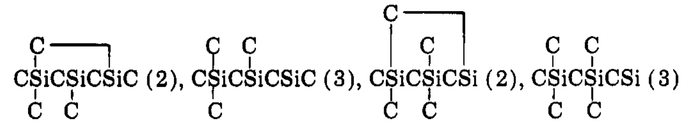
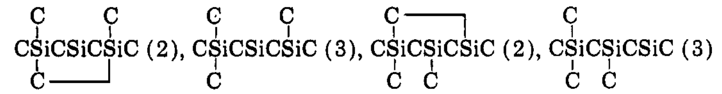
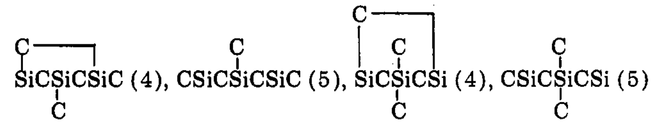
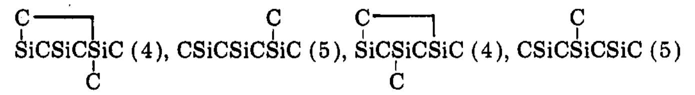
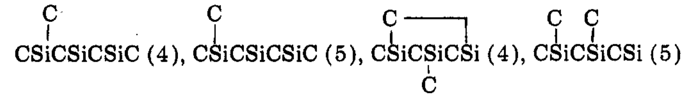
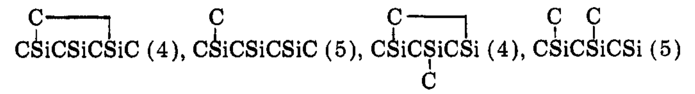


Scheme IV. Consequences of DMS Trapping of Silylsilylenes. The Generation of an Effective Multifunctionality in Silylene Intermediates

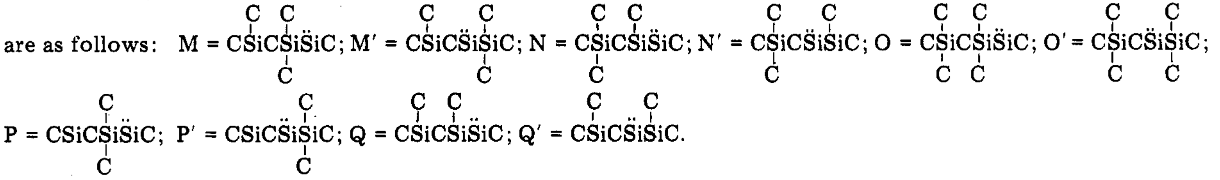


Scheme IV rationalizes the production of trimethylsilane (an important reaction product with yields of 1.5%), and it also shows how multifunctionality can be built into the higher molecular weight silylene intermediates. Thus trimethylsilyl (or dimethylsilyl) groups introduced by the BLOCK sequence can at any subsequent time be removed (by reaction b) to regenerate a silylene center. This latent multifunctionality in higher molecular weight carbo-

Table III. Tertiary Intermediates M-Q′[b] and Their 1,3,5-Trisilapentane and 1,3,5-Trisilacyclohexane Reaction Products[a]

reactant	products (no. of Si–H bonds)
M	 CSiCSiCSiC (3), CSiCSiCSiC (4), CSiCSiCSi (3), CSiCSiCSi (4)
M′	 CSiCSiCSiC (3), CSiCSiCSiC (4), CSiCSiCSiC (3), CSiCSiCSiC (4)
N	 CSiCSiCSiC (3), CSiCSiCSiC (4), CSiCSiCSi (3), CSiCSiCSi (4)
N′	 CSiCSiCSiC (3), CSiCSiCSiC (4), CSiCSiCSi (3), CSiCSiCSi (4)
O	 CSiCSiCSiC (2), CSiCSiCSiC (3), CSiCSiCSi (2), CSiCSiCSi (3)
O′	 CSiCSiCSiC (2), CSiCSiCSiC (3), CSiCSiCSiC (2), CSiCSiCSiC (3)
P	 SiCSiCSiC (4), CSiCSiCSiC (5), SiCSiCSi (4), CSiCSiCSi (5)
P′	 SiCSiCSiC (4), CSiCSiCSiC (5), SiCSiCSiC (4), CSiCSiCSiC (5)
Q	 CSiCSiCSiC (4), CSiCSiCSiC (5), CSiCSiCSi (4), CSiCSiCSi (5)
Q′	 CSiCSiCSiC (4), CSiCSiCSiC (5), CSiCSiCSi (4), CSiCSiCSi (5)

[a] Reaction paths to products (relative to their table positions): i, l, k; i, l, a, b; i, m, k; i, m, a, b. [b] Tertiary intermediates are as follows:



$\mathrm{M = C\overset{C}{Si}C\overset{C}{\underset{C}{Si}}\ddot{Si}C}$; $\mathrm{M' = C\overset{C}{Si}C\ddot{Si}\overset{C}{\underset{C}{Si}}C}$; $\mathrm{N = C\overset{C}{\underset{C}{Si}}C\overset{C}{Si}\ddot{Si}C}$; $\mathrm{N' = C\overset{C}{\underset{C}{Si}}C\ddot{Si}\overset{C}{Si}C}$; $\mathrm{O = C\overset{C}{\underset{C}{Si}}C\overset{C}{\underset{C}{Si}}\ddot{Si}C}$; $\mathrm{O' = C\overset{C}{\underset{C}{Si}}C\ddot{Si}\overset{C}{\underset{C}{Si}}C}$; $\mathrm{P = CSiC\overset{C}{\underset{C}{Si}}\ddot{Si}C}$; $\mathrm{P' = CSiC\ddot{Si}\overset{C}{\underset{C}{Si}}C}$; $\mathrm{Q = C\overset{C}{Si}C\overset{C}{Si}\ddot{Si}C}$; $\mathrm{Q' = C\overset{C}{Si}C\ddot{Si}\overset{C}{Si}C}$.

silylenes provides a very reasonable mechanistic explanation for the production of complex reaction products like the adamantanes (see Scheme V).

The Scheme V sequence can clearly occur in many ways, starting from numerous silylene intermediates, and hence a variety of adamantane products as well as still more complex products can be produced. Silylene centers, of course, would not be expected to coexist (they are too reactive). They can, however, be generated and reacted in sequence as shown.

Qualitative and Quantitative Conclusions Based on the Mechanism and Product Yield Data

Scheme VI products reveal that 1,3-disilapropanes with three Si–H bonds and 1,3-disilacyclobutanes with two Si–H bonds are the most important; Table II shows that these products follow from intermediates G and H. This is expected since dimethylsilylene (A) must be the dominant reaction intermediate [A is produced in the major primary dissociation reaction and regenerated in numerous subsequent reactions], and A produces D which in turn produces mainly G and H through reactions l and m. The fact that linear carbosilanes with two and four Si–H bonds also occur indicates that intermediates $CH_2{=}SiMe_2$ (E) leading to I and MeSiH (B) leading to J and K are also important. By the mechanism, this indicates that reaction n (forming B and E) competes with reactions l and m. The Arrhenius parameters provided for these reactions would appear to exclude such a competition (e.g., at 873 K, $k_n \approx 5 \times 10^4$, $k_m \approx 10^6$, and $k_l \approx 2 \times 10^{11}$). However, the back reactions of reactions l and m are very fast and produce near equilibrium conditions for species G and H (see Table V). Product formations from reactions l and m, therefore, are actually controlled by reactions j and a, and competition of reaction n with these reactions (according to the Arrhenius estimates) is possible. There are other experimental data supporting this "effective" reaction l, m, and n competition. Thus Gaspar et al.[28] found that the flash

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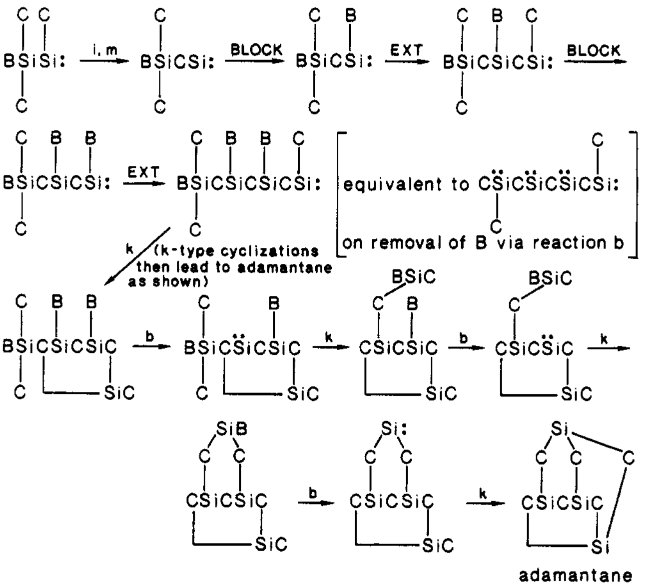
[28] Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *98*, 868.

Scheme V. Mechanism of Formation of Adamantane Type Products in the Dimethylsilane Pyrolysis (Starting with Species L)[a]



[a] B = Me_3Si- or Me_2SiH-.

pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (a system which is acknowledged to produce 1,1,2-trimethyldisilacyclopropane via reaction p) yielded three disilacyclobutane products: $Me_2Si[CH_2]_2SiH_2$, $MeHSi[CH_2]_2SiHMe$, and $Me_2Si[CH_2]_2SiHMe$. The former two are clearly products following reactions l and m, while the latter is a product following from reaction n. Hence the rapid reversibility of reactions l and m allows for product formations from all three reaction channels of trimethyldisilacyclopropane.

The Scheme VI product data provides semiquantitative information on several reaction competitions.

(1) According to the mechanism, secondary intermediate hydrogenation to 1,3-disilapropanes (DSP) competes with tertiary intermediate production which ultimately leads to higher carbosilane products (HCP) of three or more Si atoms. This competition is between reaction b and reaction c + d. From the product yields, $Y(DSP)/Y(HCP) \approx rate(b)/rate(c + d) \approx 2.3$.

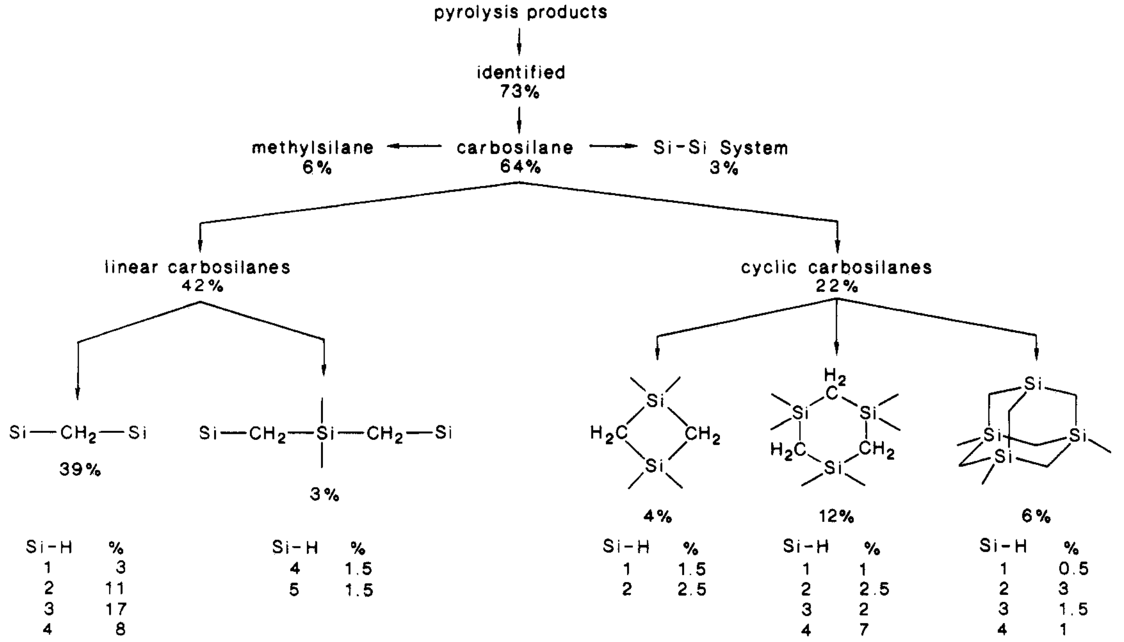
(2) Yields of 1,3-disilapropanes (DSP, 39%) are about an order of magnitude higher than yields of 1,3-disilacyclobutanes (DSCB, 4%). These are products of competing reaction paths (reaction a + b vs reaction j). Hence, $\text{yield(DSP)}/\text{yield(DSCB)} = 9.75 = [k_a k_b/(k_{-a} + k_b)][DMS]/k_j = k_a[DMS]/2k_j$ (since $k_{-a} \approx k_b$). With [DMS] = 200 Torr, T = 870 K, $A_j = 10^{12.0}$ s^{-1}, and $k_a = 10^{9.5}$ M^{-1} s^{-1}, one obtains an average E_j = 30.8 kcal. This value can be compared to the activation energies of bimolecular silylene insertions into the C–H bonds of methane: $E_{act}(SiH_2 + CH_4 \rightarrow CH_3SiH_3) = 17.9 \pm 2$ kcal and $E_{act}(MeSiH + CH_4 \rightarrow DMS) = 22.9 \pm 2$ kcal. [These values come from the activation energies for methane elimination in the decompositions of $MeSiH_3$ (68 kcal)[22] and Me_2SiH_2 (73 kcal)[5] and their respective reaction enthalpies.[23] By extrapolation of the apparent Me replacement for H effect, one obtains $E_{act}(Me_2Si\colon + CH_4) \approx 27.9$ kcal, which is in fair agreement with the above estimated E_j considering the fact that the latter may be higher than the former because of the development of ring strain in the cyclic transition state.

Reaction Modeling

The complete DMS pyrolysis reaction system is far too complex to model. However, by focusing on a representative collection of the most important reactions, it is possible to show through the modeling that the reactions and schemes proposed here provide a reasonable semiquantitative interpretation of the reaction system. The reactions considered in the modeling, along with their assigned Arrhenius parameters, are shown in the Table V. Reaction types a–m are represented; reaction types o–q are too slow to compete at the relatively high reactant concentrations employed.[1] A discussion of some of the Arrhenius parameter assignments is needed, and this is given below.

1. Alkyldisilane Decompositions Generating R_2Si Species. Davidson et al.[29] have determined the decom-

Scheme VI. Pyrolysis Products of Me_2SiH_2



position kinetics of pentamethyldisilane and 1,1,2-trimethyldisilane (log k (s^{-1}) = 12.93 − 47.3/θ and log k (s^{-1}) = 12.56 − 46.0/θ, respectively, where $\theta = 2.303RT$). In the modeling, we have assigned parameters consistant with log k (s^{-1}) = 12.9 − 48.0/θ to all disilane eliminations producing R_2Si: species.

2. Silylene Insertions into Si–H Bonds. We have assumed zero activation energies for the Si–H insertion reactions of all silylenes. Laser-excited fluorescence measurements[30] of the rate constants for SiH_2 insertions into Si–H bonds of silanes are in the range $10^{10.6 \bullet 0.2}$ M^{-1} s^{-1}. The calculated A factor for SiH_2 insertion into SiH_4[31] (from the disilane decomposition experimental high-pressure A factor and reaction entropy) is $10^{10.4}$ M^{-1} s^{-1}. This is close to the LEF rate constant result and supports the zero activation energy assumption. For Me_2Si, Si–H bond insertion rate constants from laser absorption (LA) measurements give values ranging from $10^{8.1}$ (reaction with SiH_4)[32] to $10^{9.5}$ M^{-1} s^{-1} (reaction with Me_2SiH_2).[32] Calculations of the A factors of these Me_2Si insertion reactions, from the entropies and the experimental Arrhenius parameters of their reverse decomposition reactions at 600 K (i.e., $\Delta S°_{DMDS} \approx 31.7$ and $\Delta S°_{TMDS} \approx 32.6$ cal/deg;[34] $A_{DMDS} \approx 10^{12.7}$ s^{-1} [33] and $A_{TMDS} \approx 10^{13.3}$ s^{-1};[25] DMDS = 1,1 dimethyldisilane and TMDS = 1,1,2,2 tetramethyldisilane) give $10^{8.2}$ M^{-1} s^{-1} for the insertion of Me_2Si into silane (in good agreement with the LA measurement) and $10^{8.3}$ M^{-1} s^{-1} for the insertion of Me_2Si into dimethylsilane (in poor agreement with the LA value). There are no absolute rate constant data for MeSiH insertions into Si–H bonds, but similar calculations from the reported decomposition kinetics of the product disilanes suggest that methylsilylene has reactivities intermediate to those of silylene and dimethylsilylene. Thus the calculated A factors for MeSiH insertions into silane[35] and dimethylsilane[29] are $10^{9.3}$ and $10^{8.5}$ M^{-1} s^{-1}, respectively. There are also no data available on larger silylene insertions into Si–H bonds (i.e., RSiR′, where R > Me), although one would expect that steric effects would lower insertion rates relative to their methylated counterparts. Because of the uncertainties involved in these rate constants, we have assigned all dialkylsilylene insertions into the Si–H of DMS values of 10^{8} M^{-1} s^{-1} and values about 7 times higher for all monoalkylsilylene Si–H insertions with DMS. If anything, these assignments are on the low side and act in the modeling to reduce the predicted yields of the higher molecular weight products. Fitting the high yields observed for these products is the most difficult mechanistic challenge of the modeling, and the fact that the proposed mechanism meets this challenge, even with the low Si–H insertion rate constants assigned, provides additional support for the mechanism. It should be noted that modeling was also done with insertion rate constants 20 times larger. Equally good fits to the data were realized when compensating adjustments in the rate constants of competing reactions were made.

3. Intramolecular Silylene C–H Insertion Activation Energies. It is evident that activation energies for silylene insertions into C–H bonds increase in value by about 3–5 kcal with each alkyl group replacement of H on the reacting silylene (loc. cit.). Activation energy limits for these reactions can be set relative to the experimental values for insertions into the C–H of CH_4. Thus for RSiH species, the limits are between 24 and 30 kcal for disilacyclobutane forming reactions and 17–23 kcal for trisilacyclohexane forming reactions, while for R_2Si species the limits are between 28 and 34 kcal for the former and between 22 and 28 kcal for the latter. These limits assume ring strains of 6 and 0 kcal in the cyclic transition states of the four- and six-membered product forming reactions, respectively, and are uncertain to the extent of the energy lowering which could result because the insertions of interest are into the C–H of methyl rather than the C–H of methane (a 6 kcal/mol difference). The activation energies assigned to the various cyclizations in our modeling fall in the ranges of the above estimates.

Table IV. Modeling Results for the Appendix Modified Mechanism

	product types[a]			
	DSPr	DScyBu	TSHex	TscyHex
exptl (%)	39	4	3	12
calcd (%)[f]	34.2	2.0	0.53	2.7
calcd (%)[g]	39.1[b]	4.9[c]	0.95[d]	9.9[e]

[a] DSPr = product yields of all disilapropanes; DScyBu = product yields of all disilacyclobutanes; TSHex = product yields of all trisilahexanes; TScyHex = product yields of all trisilacyclohexanes. [b] P2 = 20.1%, P6 = 19.0% (see Table V for P identifications). [c] P1 = 2.30%, P5 = 2.63%. [d] P4 = 0.34%, P8 = 0.41%, P9 = 0.15%, P10 = 0.04%. [e] P3 = 4.15%, P7 = 5.27%. [f] First pass products of reaction with $t_{residence} = 50$ s, $T = 873$ K, and [A] = 3.7×10^{-3} M. [g] Products produced from approximate steady-state reactant input concentrations (i.e. dimethylsilane at 200-Torr pressure, P2 at 11-Torr pressure, and P6 at 5.5-Torr pressure; see discussion).

4. Disilacyclopropane Ring-Opening Reactions. Disilacyclopropane ring-opening reactions in our schemes occur by H migration (reaction type l) or by methyl migration (reaction type m). The ring strain assist in ring opening is not known; however the difference in activation energy between these two processes can be estimated from the 67 ± 2 kcal activation energy for hexamethyldisilane decomposition to tetramethylsilane[36] (an unstrained Me migration Si–Si bond-breaking process) and the 50 ± 3 kcal activation energies reported for various disilane decompositions (unstrained H migration Si–Si bond-breaking processes). Thus Me migration ring openings should have activation energies 17 ± 5 kcal higher than H migration ring openings.

Modeling Results

The results of the modeling are shown in Table IV. Two sets of results are shown. One shows the product yields (based on dimethylsilane loss) after a single pass through the 1-m reactor at 600 K; the second shows the product yields produced under what we estimate to be steady-state reactant conditions. The main carbosilane products of a single pass through the reactor are disilapropanes. These species have significant vapor pressures at room temperature (i.e. the product collection trap temperature) and therefore must have been recirculated (along with the reactant) at pressures close to their room-temperature vapor pressures. While the recirculated gases also passed through a −45 °C trap holding reactant, the apparatus diagram of ref 1 suggests that flux of reactant from

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Table V. Modified $\mathrm{Me_2SiH_2}$ Pyrolysis Mechanism and Rate Constants[a]

reaction	log *A*		*E*, kcal
$\mathrm{DMS \xrightarrow{1} Me_2\ddot{Si} + H_2}$	14.3		68.0
$\mathrm{DMS + Me_2\ddot{Si} \underset{3}{\overset{2}{\rightleftharpoons}} Me_2SiHSiHMe_2}$	8.0 12.9		0.0 48.0
$\mathrm{Me_2SiHSiHMe_2 + Me_2\ddot{Si} \xrightarrow{4} DMS + Me_2Si{=}SiMe_2}$		$k_4 = k_2$	
$\mathrm{Me_2Si{=}SiMe_2 \underset{6}{\overset{5}{\rightleftharpoons}} Me_3Si\ddot{Si}Me}$	13.4 12.9		43.0 38.0
$\mathrm{Me_3Si\ddot{Si}Me \underset{9}{\overset{8}{\rightleftharpoons}} Me_2\underbrace{Si{-}Si}_{CH_2}HMe}$	12.9 13.4		32.0 36.4
$\mathrm{Me_2\underbrace{Si{-}Si}_{CH_2}HMe \underset{11}{\overset{10}{\rightleftharpoons}} Me_2SiHCH_2\ddot{Si}Me}$	13.7 12.0		8.0 10.0
$\mathrm{\underset{13}{\overset{12}{\rightleftharpoons}} Me_3SiCH_2\ddot{Si}H}$	13.0 11.7		24.0 25.0
$\mathrm{Me_2SiHCH_2\ddot{Si}Me \xrightarrow{14} Me\underbrace{SiHCH_2Si}_{CH_2}HMe\ (P1)}$	12.0		34.0
$\mathrm{+ DMS \underset{16}{\overset{15}{\rightleftharpoons}} Me_2SiHCH_2SiMeHSiHMe_2}$		$k_{15} = k_2$ $k_{16} = k_3$	
$\mathrm{Me_2SiHCH_2SiMeHSiHMe_2 \underset{18}{\overset{17}{\rightleftharpoons}} Me_2\ddot{Si} + Me_2SiHCH_2SiH_2Me\ (P2)}$		$k_{17} = k_3$ $k_{18} = k_2$	
$\mathrm{+ Me_2\ddot{Si} \xrightarrow{19} Me_2SiHCH_2SiMe{=}SiMe_2 + DMS}$		$k_{19} = k_2$	
$\mathrm{Me_2SiHCH_2SiMe{=}SiMe_2 \underset{21}{\overset{20}{\rightleftharpoons}} Me_2SiHCH_2SiMe_2\ddot{Si}Me}$	13.1 13.0		43.0 38.0
$\mathrm{Me_2SiHCH_2SiMe_2\ddot{Si}Me \underset{23}{\overset{22}{\rightleftharpoons}} Me_2SiHCH_2\underbrace{SiMe{-}Si}_{CH_2}HMe}$	12.7 13.4		32.0 36.4
$\mathrm{Me_2SiHCH_2\underbrace{SiMe{-}Si}_{CH_2}HMe \underset{26}{\overset{25}{\rightleftharpoons}} Me_2SiHCH_2SiMeHCH_2\ddot{Si}Me}$		$k_{25} = k_{10}$ $k_{26} = k_{11}$	
$\mathrm{\underset{28}{\overset{27}{\rightleftharpoons}} Me_2SiHCH_2SiMe_2CH_2\ddot{Si}H\ (W)}$		$k_{27} = k_{12}$ $k_{28} = k_{13}$	
$\mathrm{Me_2SiHCH_2SiMeHCH_2\ddot{Si}Me \xrightarrow{29} Me\underbrace{SiHCH_2SiMeHCH_2Si}_{CH_2}HMe\ (P3)}$	10.8		22.0
$\mathrm{+ DMS \underset{31}{\overset{30}{\rightleftharpoons}} RSiHMeSiHMe_2}$		$k_{30} = k_2$ $k_{31} = k_3$	
$\mathrm{RSiHMeSiHMe_2 \underset{33}{\overset{32}{\rightleftharpoons}} Me_2\ddot{Si} + Me_2SiHCH_2SiMeHCH_2SiH_2Me\ (P4)}$		$k_{32} = k_3$ $k_{33} = k_2$	
$\mathrm{Me_3SiCH_2\ddot{Si}H \xrightarrow{34} Me_2\underbrace{SiCH_2Si}_{CH_2}H_2\ (P5)}$	12.0		31.0
$\mathrm{+ DMS \underset{36}{\overset{35}{\rightleftharpoons}} Me_3SiCH_2SiH_2SiHMe_2}$		$k_{35} = 7k_2$ $k_{36} = k_3$	
$\mathrm{Me_3SiCH_2SiH_2SiHMe_2 \underset{38}{\overset{37}{\rightleftharpoons}} Me_2\ddot{Si} + Me_3SiCH_2SiH_3\ (P6)}$		$k_{37} = k_3$ $k_{38} = k_2$	
$\mathrm{+ Me_2\ddot{Si} \xrightarrow{39} Me_3SiCH_2SiH{=}SiMe_2 + DMS}$		$k_{39} = k_2$	
$\mathrm{Me_3SiCH_2SiH{=}SiMe_2 \underset{41}{\overset{40}{\rightleftharpoons}} Me_3SiCH_2\ddot{Si}SiMe_2H}$	12.8 12.8		30.0 25.0
$\mathrm{Me_3SiCH_2\ddot{Si}SiMe_2H \underset{43}{\overset{42}{\rightleftharpoons}} Me_3SiCH_2\underbrace{SiH{-}Si}_{CH_2}HMe}$	12.9 13.4		32.0 36.4
$\mathrm{Me_3SiCH_2\underbrace{SiH{-}Si}_{CH_2}HMe \underset{45}{\overset{44}{\rightleftharpoons}} Me_3SiCH_2SiH_2CH_2\ddot{Si}Me\ (Q)}$		$k_{44} = k_{10}$ $k_{45} = k_{11}$	
$\mathrm{\underset{47}{\overset{46}{\rightleftharpoons}} Me_3SiCH_2SiHMeCH_2\ddot{Si}H\ (P)}$		$k_{46} = k_{12}$ $k_{47} = k_{13}$	
$\mathrm{Q \xrightarrow{48} Me_2\underbrace{SiCH_2SiH_2CH_2Si}_{CH_2}HMe\ (P7)}$		$k_{48} = k_{29}$	
$\mathrm{P \xrightarrow{49} Me_2\underbrace{SiCH_2SiHMeCH_2Si}_{CH_2}H_2\ (P7)}$	10.8		17.0
$\mathrm{Q + DMS \underset{51}{\overset{50}{\rightleftharpoons}} Me_3SiCH_2SiH_2CH_2SiHMeSiHMe_2\ (S)}$		$k_{50} = k_2$ $k_{51} = k_3$	
$\mathrm{S \underset{53}{\overset{52}{\rightleftharpoons}} Me_2\ddot{Si} + Me_3SiCH_2SiH_2CH_2SiH_2Me\ (P8)}$		$k_{52} = k_3$ $k_{53} = k_2$	
$\mathrm{P + DMS \underset{55}{\overset{54}{\rightleftharpoons}} Me_3SiCH_2SiHMeCH_2SiH_2SiHMe_2\ (T)}$		$k_{54} = 7k_2$ $k_{55} = k_3$	
$\mathrm{T \underset{57}{\overset{56}{\rightleftharpoons}} Me_2\ddot{Si} + Me_3SiCH_2SiHMeCH_2SiH_3\ (P9)}$		$k_{56} = k_3$ $k_{57} = k_2$	
$\mathrm{W \xrightarrow{58} Me\underbrace{SiHCH_2SiMe_2CH_2Si}_{CH_2}H_2\ (P7)}$		$k_{58} = k_{49}$	
$\mathrm{W + DMS \underset{60}{\overset{59}{\rightleftharpoons}} Me_2SiHCH_2SiMe_2CH_2SiH_2SiHMe_2\ (U)}$		$k_{59} = 7k_2$ $k_{60} = k_3$	
$\mathrm{U \underset{62}{\overset{61}{\rightleftharpoons}} Me_2\ddot{Si} + Me_2SiHCH_2SiMe_2CH_2SiH_3\ (P10)}$		$k_{61} = k_3$ $k_{62} = k_2$	

[a] In the above, DMS = $\mathrm{Me_2SiH_2}$, R = $\mathrm{Me_2SiHCH_2SiMeHCH_2}$–, and products are identified by P*n* (*n* = 1–10).

this bath could well prevent complete condensation of the disilapropanes. We assumed that roughly half of the disilapropane products entering the −45 °C trap passed the trap and were recirculated. The modeling results on this basis are in good agreement with the reported overall yield data (see Table IV). It is clear, from the modeling, that the proposed mechanism is a reasonable one, both qualitatively and quantitatively. While the modeling could be extended and better fits realized, such an exercise would not be instructive at this time as there are far too many unknowns in the rate constant assignments. Clearly the pressing need now is for more and better data on the elementary reactions of silylenes.

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Registry No. Me_2SH_2, 1111-74-6; $Me_2S:$, 6376-86-9; $Me_2SiHCH_2SiH_2Me$, 18148-13-5; $MeSiHCH_2SiHMeCH_2$, 1628-01-9; $Me_3SiCH_2SiH_3$, 18148-12-4; $Me_2SiCH_2SiH_2CH_2$, 38512-90-2; $Me_3SiCH_2SiH_2Me$, 18163-83-2; $Me_2SiCH_2SiHMeCH_2$, 25261-26-1; $MeSiH_2CH_2SiH_2Me$, 5654-05-7; $SiH_2CH_2SiHMeCH_2$, 80540-80-3; $Me_2SiHCH_2SiH_3$, 18145-47-6.

The Mechanism of the Formation of Silyl Enol Ethers from Hydrosilanes and Organic Carbonyl Compounds in the Presence of Cobalt Carbonyls. Kinetic Investigation of Some Reaction Steps

István Kovács,† Attila Sisak,‡ Ferenc Ungváry,† and László Markó*†

Institute of Organic Chemistry, University of Veszprém, H-8200 Veszprém, Hungary, and Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém, Hungary

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The cleavage of isobutyrylcobalt tetracarbonyl with triethylsilane gives (triethylsilyl)cobalt tetracarbonyl, isobutyraldehyde, dicobalt octacarbonyl, and the corresponding unsaturated and saturated silyl ethers. Silyl enol ether was also formed, along with order products, in the reaction of (trimethylsilyl)cobalt tetracarbonyl with isobutyraldehyde. The kinetics of both reactions were studied. The first one proceeds through an acylcobalt tricarbonyl intermediate that oxidatively adds hydrosilane in the rate-determining step and then gives the products in fast consecutive steps. The second reaction involves probably an (α-(trimethylsiloxy)isobutyl)cobalt tetracarbonyl intermediate formed from silylcobalt tetracarbonyl and aldehyde. Silyl enol ethers as main products will be provided by β-hydrogen elimination from α-siloxyalkyl complexes in both reactions.

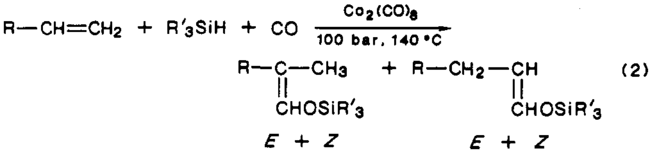
Introduction

The formation of silyl enol ethers from ketones and hydrosilanes in good yields in the presence of dicobalt octacarbonyl and amines was described some years ago (eq 1)[1] ($RCH_2C(O)R'$ = aliphatic, cycloaliphatic, or alkyl-

$$RCH_2C(O)R' + R''_3SiH \xrightarrow[50\ °C]{Co_2(CO)_8/L} RCH{=}C(R')OSiR''_3 + H_2 \quad (1)$$

aromatic ketone; R''_3SiH = trialkyl-, aryldialkyl-, or trialkoxysilane; L = amine). Without use of an amine, a mixture of $RCH{=}C(R')OSiR''_3$ and $RCH_2CH(R')OSiR''_3$ results.

The mechanism of this interesting process has not been discussed. More detailed studies were conducted by Murai and co-workers[2] to the "siloxymethylenylation" of alkenes and cycloalkenes, which was regarded as an analogue of the hydroformylation process (eq 2). The mechanistic proposals made by the authors at that time were necessarily based on rather scanty information regarding the formation and reactivity of silylcobalt carbonyl complexes[3,4] and thus need reexamination. For example, it was shown recently that reaction 3, which was proposed to be the first step of reaction 2, actually did not take place but that $R_3SiCo(CO)_4$ and H_2 are the only products in the reaction between $Co_2(CO)_8$ and R_3SiH (eq 4).[6]



$$R{-}CH{=}CH_2 + R'_3SiH + CO \xrightarrow[100\ bar,\ 140\ °C]{Co_2(CO)_8} R{-}C(CH_3){=}CHOSiR'_3\ (E+Z) + R{-}CH_2{-}CH{=}CHOSiR'_3\ (E+Z) \quad (2)$$

$$Co_2(CO)_8 + R_3SiH \rightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \quad (3)$$

$$Co_2(CO)_8 + 2R_3SiH \rightarrow 2R_3SiCo(CO)_4 + H_2 \quad (4)$$

We have recently determined the kinetics of the cleavage of *n*-butyrylcobalt tetracarbonyl and isobutyrylcobalt tetracarbonyl with H_2 and $HCo(CO)_4$ and proposed a mechanism[7] for these reactions that form a part of the catalytic hydroformylation cycle of propene. The present

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† University of Veszprém.

‡ Research Group for Petrochemistry of the Hungarian Academy of Sciences.

[1] Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* 1977, 2671.

[2] (a) Seki, Y.; Hidaka, A.; Makino, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* 1977, *140*, 361. (b) Seki, Y.; Murai, S.; Hidaka, A.; Sonoda, N. *Angew. Chem.* 1977, *89*, 919. (c) Murai, S.; Sonoda, N. *Angew. Chem.* 1979, *91*, 896.

[3] E.g.; Harrod, J. F.; Chalk, A. J. In *Organic Syntheses Via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 687–692 and references therein.

[4] Important mechanistic details even about the well-documented hydroformylation reaction became known only in the eighties.[5]

[5] Ungváry, F.; Markó, L. *J. Organomet. Chem.* 1981, *219*, 397. Markó, L. *Fundament. Res. Homogen. Catal.* 1984, *4*, 1.

[6] Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* 1986, *5*, 1019.

[7] Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* 1986, *5*, 209.