Kinetics of the Formation of Silylenes from Some Disilanes

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The kinetics of the gas-phase pyrolytic formation of silylenes from 1,2-dimethoxytetramethyldisilane, methoxypentamethyldisilane, 1-methoxy-1-propyltetramethyldisilane, and 1,2-dimethyldisilane have been measured. The results are discussed in relation to substituent effects on bond dissociation energies, the energetics of silylene insertion reactions, and intramolecular reactions of silylenes.

Introduction

It has long been known that disilanes with at least one hydrogen, halogen, or alkoxy group attached to silicon give silylenes instead of silyl radicals on pyrolysis;[1] e.g., in the pyrolysis of pentamethyldisilane elimination of dimethylsilylene by a 1,2-hydrogen shift from silicon to silicon (reaction 1) is favored over homolysis (reaction 2), whereas for hexamethyldisilane the reverse is the case, silyl radical formation by reaction 4 being favored over silylene formation by reaction 3. This has been explained[2] in

$$\mathrm{Me_3SiSiMe_2H \rightarrow Me_2Si\!: + Me_3SiH} \quad (1)$$

$$[\mathrm{Me_3SiSiMe_2H \rightarrow Me_3Si^\bullet + HMe_2Si^\bullet}] \quad (2)$$

$$[\mathrm{Me_3SiSiMe_3 \rightarrow Me_2Si\!: + Me_4Si}] \quad (3)$$

$$\mathrm{Me_3SiSiMe_3 \rightarrow Me_3Si^\bullet + Me_3Si^\bullet} \quad (4)$$

terms of the interplay between thermodynamic and kinetic effects in which the key factor is the size of the activation energies for the reverse reactions (−1) and (−3). Since silylenes insert easily into silicon–hydrogen bonds but require a substantial activation energy to insert into silicon–methyl, E_{-1} is small while E_{-3} is large. silylene formation is thermodynamically favored in both cases; i.e., $\Delta H_1 < \Delta H_2$ and $\Delta H_3 < \Delta H_4$. Since E_{-1} and E_{-2} are both small, the activation energies for pentamethyldisilane reflect ΔH; i.e., $E_1 < E_2$. However, in the case of hexamethyldisilane the large E_{-3} pushes E_3 above E_4. As silylenes also insert readily into silicon–halogen and silicon–alkoxy bonds, disilanes containing such bonds are likewise good thermal sources of silylenes. Ever since the seminal work of Atwell and Weyenberg on methoxydisilanes,[1] this feature of disilane chemistry has been put to good use in generating silylenes,[3] but despite the importance of methoxydisilanes as silylene sources no kinetic studies of them have been reported other than a few measurements in solution on 1,2-dimethoxytetramethyldisilane (I).[4] Arrhenius parameters have been measured in the gas phase for the formation of silylenes from a number of hydrido-[5–7] and chlorodisilanes,[8] but these studies were undertaken before the importance in silylene chemistry of such subtleties as 1,2-hydrogen shifts in alkylsilylenes[9–11] and the involvement of disilacyclopropane intermediates[11–13] were appreciated. These considerations prompted us to investigate the kinetics of the gas-phase pyrolysis of three methoxydisilanes, viz., I, methoxypentamethyldisilane (II), and 1-methoxy-1-propyltetramethyldisilane (III), and of 1,2-dimethyldisilane (IV), which is known[14] to give methylsilylene on pyrolysis (eq 5).

$$\mathrm{H_2MeSiSiMeH_2 \rightarrow HMeSi\!: + MeSiH_3} \quad (5)$$

Results

Each compound was studied by two complementary kinetic techniques: low-pressure pyrolysis with analysis by quadrupole mass spectrometry (LPP)[15] and batch stirred flow in a carrier gas of dried deoxygenated nitrogen at ca. 1000 torr with analysis by gas chromatography (SFR).[16] Product identification was verified by GC/mass spectrometry.

As expected from earlier work,[1,4,14] preliminary experiments showed that secondary bimolcular reactions occurred readily with all compounds. For instance, pyrolysis of II at 400 °C gave ca. 30% of the trisilane and ca. 10% of the tetrasilane resulting from insertion of dimethylsilylene into silicon–oxygen bonds. Some pyrolyses were done with a view to obtaining information about some of these secondary reactions, but in order to obtain as reliable kinetic data as possible for primary silylene-forming processes, small partial pressures of each compound except III were pyrolyzed in the presence of excess 1,3-butadiene to suppress secondary reactions of silylenes. under these conditions the pyrolysis products were those expected from silylene eliminations analogous to reaction 1, viz., monosilanes and silacyclopentenes resulting from addition of dimethylsilylene (compounds I and II) or methylsilylene (compound IV) to butadiene. The adduct from dimethylsilylene was mainly 1,1-dimethylsilacyclopent-3-ene, with ≤10% 1,1-dimethylsilacyclopent-2-ene; the adduct from methylsilylene gave only one peak on the GC. We did fewer experiments on the pyrolysis of III, omitting butadiene trapping because our main interest was in the rapid elimination of propene[17] from the methylpropyl-

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Table I. Pyrolysis of Disilanes—Kinetic Results

silane	method	temp/°C	P_0/torr[a]		Kin[b]	log *A*	*E*/kcal·mol^{-1}	$k_{350°C}$/s^{-1}
I	LPP	312–379	0.2	×10	D	12.7 ± 0.2	40.2 ± 0.5	3.8 × 10^{-2}
I	SFR	304–402	0.1	×20	M	12.7 ± 0.2	38.7 ± 0.5	1.3 × 10^{-1}
I	SFR	304–402	0.1	×20	A	12.7 ± 0.2	38.6 ± 0.5	1.3 × 10^{-1}
II	LPP	391–451	4		D	11.5 ± 0.5	40.4 ± 1.5	2.2 × 10^{-3}
II	LPP	391–451	0.6	×5	D	12.6 ± 0.3	44.6 × 1.0	9.8 × 10^{-4}
II	SFR	339–448	0.6		M	12.6 ± 0.3	44.2 ± 1.7	1.4 × 10^{-3}
II	SFR	400–460	0.6	×5	M	12.7 ± 0.2	44.5 ± 0.5	1.2 × 10^{-3}
III	LPP	394–450	0.2	×10	D	11.7 ± 0.5	42.0 ± 1.5	9.5 × 10^{-4}
III	LPP	347–454	0.1		D	11.5 ± 0.2	41.1 ± 0.5	1.3 × 10^{-3}
III	SFR	320–450	1.0		M	12.7 ± 0.1	43.6 ± 0.3	2.5 × 10^{-3}
III	SFR	320–450	1.0		P	12.6 ± 0.1	43.3 ± 0.3	2.4 × 10^{-3}
IV	SFR	371–441	1.0	×50	M	14.3 ± 0.2	47.9 ± 0.6	3.1 ± 10^{-3}
IV	SFR	371–441	1.0	×50	A	14.3 ± 0.2	47.9 ± 0.6	3.1 × 10^{-3}
IV	LPP	362–444	0.2	×10	D	14.3 ± 0.2	48.7 ± 0.5	1.6 × 10^{-3}
IV	LPP	362–444	0.2	×10	A	14.5 ± 0.2	49.3 ± 0.5	1.5 × 10^{-3}

[a] "P_0/torr" gives the partial pressure in torr of the disilane. [b] "Kin" describes the type of kinetic measurement: D, decomposition of reactant; M, formation of a monosilane; A, formation of adduct between :SiMeR (R = Me, H) and butadiene; P, formation of propene.

silylene produced initially (eq 6 and 7). As expected, propene was indeed a major product in the pyrolysis of III.

$$\mathrm{Me_3SiSiMePrOMe \rightarrow PrMeSi{:} + Me_3SiOMe} \quad (6)$$

$$\mathrm{PrMeSi{:} \rightarrow HMeSi{:} + CH_3CH{=}CH_2} \quad (7)$$

The SFR technique provides kinetic data for the formation of products, while the LPP technique can measure either the kinetics of decomposition of reactant or the kinetics of formation of products. Measurement of the kinetics of formation of products by either technique requires authentic samples of products for calibration.

All of the kinetic data obtained in the light of the foregoing factors are in Table I, together with the conditions of temperature and pressure for each compound. The kinetic processes in Table I were all shown to be first order by varying the initial partial pressure of each disilane by a factor of 10; the *A* factors in Table I are therefore in s^{-1}. Arrhenius parameters were measured at the constant partial pressures listed in Table I. Compound IV was also pyrolyzed in the absence of butadiene to obtain information about secondary products. These pyrolyses were done in the SFR with analysis by gas chromatography and in a similar apparatus attached to a GC/mass spectrometer. As expected, pyrolysis between 371 and 453 °C gave $\mathrm{MeSiH_3}$ and $\mathrm{H_2MeSiSiMeHSiMeH_2}$, the first insertion product of :SiMeH into a silicon–hydrogen bond in IV, but there were also very small quantities of other trisilanes, tetrasilanes, and higher polysilanes. At higher pyrolysis temperatures the next most abundant product after $\mathrm{MeSiH_3}$ was $\mathrm{Me_2SiH_2}$. As this product had not been reported previously[14] and is of some mechanistic interest, we were careful to identify it by comparison of gas chromatographic retention time with an authentic sample of $\mathrm{Me_2SiH_2}$ and by GC/mass spectrometry. At 453 °C, $[\mathrm{MeSiH_3}]:[\mathrm{H_2MeSiSiMeHSiMeH_2}]:[\mathrm{Me_2SiH_2}] \simeq 1{:}\leq 0.04{:}0.1$. As the temperature was reduced, the trisilane concentration increased while $[\mathrm{Me_2SiH_2}]$ decreased; the ratios at 382 °C were $1{:}\leq 0.64{:}0.016$. It was difficult to obtain reliable kinetic data for the formation of such a minor product as $\mathrm{Me_2SiH_2}$, but approximate Arrhenius parameters were substantially different from those for IV in Table I, consistent with $\mathrm{Me_2SiH_2}$ being a secondary product.

Discussion

Our SFR and LPP techniques were designed to be exceptionally economical in material, allowing worthwhile kinetic studies to be undertaken on compounds only available in small quantities. Furthermore, the LPP technique produces voluminous kinetic data rapidly, but there are inevitably compensating drawbacks. Low-pressure conditions minimize secondary bimolecular reactions, thus facilitating study of primary processes, but if the pressure is reduced too much, the measured Arrhenius parameters may be affected by unimolecular falloff. LPP is a "static" technique in which a pyrolysis is continuously monitored by leaking a small portion of the reaction mixture into the mass spectrometer. This leakage is measured below pyrolysis temperature for each compound studied, and rate constants corrected accordingly. Obviously, the reliability of these corrected rate constants decreases as the rate constants decrease so that the correction is no longer small. There is also a limitation on high rate constants, which will be underestimated if the time scale of a pyrolysis is short compared to the time taken for the reactant to enter the reaction vessel at the start of a run. These combined constraints limit LPP to measuring first-order rate constants between ca. 5 × 10^{-4} and 2 × 10^{-1} s^{-1}. The batch SFR technique suffers no disadvantage relative to conventional continuous flow techniques for first-order reactions, but kinetic analysis of data is more complicated for reactions of higher order.[16] In addition to these special features, both LPP and SFR are as dependent on analytical methods as any other kinetic technique; gas chromatographic or mass spectrometric peaks used as measures of the concentration of a reactant or product should be unique and well-resolved, or adequately corrected if that is not possible. It is therefore prudent to measure kinetics by a variety of methods and to compare critically the resulting Arrhenius parameters within each pyrolysis study. If there are discrepancies that cannot otherwise be explained, SFR results should probably be preferred, because that technique is more straightforward than LPP, as explained above.

It is clear from earlier work[1,4,14] and from this that silylene elimination was the primary reaction in each of these pyrolyses, thus

$$\underset{\text{I}}{\mathrm{MeOMe_2SiSiMe_2OMe}} \rightarrow \mathrm{Me_2Si{:} + M_2Si(OMe)_2} \quad (8)$$

$$\underset{\text{II}}{\mathrm{Me_3SiSiMe_2OMe}} \rightarrow \mathrm{Me_2Si{:} + Me_3SiOMe} \quad (9)$$

$$\underset{\text{III}}{\mathrm{Me_3SiSiMePrOMe}} \rightarrow \mathrm{PrMeSi{:} + Me_3SiOMe} \quad (6)$$

$$\underset{\text{IV}}{\mathrm{H_2MeSiSiMeH_2}} \rightarrow \mathrm{HMeSi{:} + MeSiH_3} \quad (5)$$

In the pyrolysis of I with excess butadiene by SFR, excellent agreement was obtained between the Arrhenius parameters for the formation of dimethyldimethoxysilane and 1,1-dimethylsilacyclopentene, as expected for reaction 8. These are our preferred Arrhenius parameters for k_8,

Table II. Arrhenius Parameters for Formation of Dimethylsilylene

reaction	log A	E/kcal	$k_{350^\circ\mathrm{C}}$/s^{-1}	ref
$\mathrm{Me_3SiSiMe_2Cl \xrightarrow{10} Me_3SiCl + {:}SiMe_2}$	11.7 ± 0.3	50.1 ± 1.1	1.3×10^{-6}	8
$\mathrm{Me_3SiSiMe_2H \xrightarrow{1} Me_3SiH + {:}SiMe_2}$	12.9 ± 0.3	47.4 ± 1.0	1.9×10^{-4}	7, *a*
$\mathrm{HMe_2SiSiMeH_2 \xrightarrow{11} MeSiH_3 + {:}SiMe_2}$	12.6 ± 2	46 ± 5	2.9×10^{-4}	7
$\mathrm{Me_3SiSiMe_2OMe \xrightarrow{9} Me_3SiOMe + {:}SiMe_2}$	12.7 ± 0.2	44.5 ± 0.5	1.2×10^{-3}	*b*
$\mathrm{MeOMe_2SiSiMe_2OMe \xrightarrow{8} Me_2Si(OMe)_2 + {:}SiMe_2}$	12.7 ± 0.2	39 ± 1.5	1.0×10^{-1}	*b*

[a] This pyrolysis has very recently been repeated here by M. P. Clarke, using the same SFR technique as was used in this work. Pyrolyses with a 10-fold excess of 2,3-dimethylbutadiene between 410 and 470 °C gave Arrhenius parameters for formation of $\mathrm{Me_3SiH}$ (log A = 13.3 ± 0.1, E = 48.4 ± 0.3 kcal) and the $\mathrm{{:}SiMe_2}$ adduct (log A = 13.1 ± 0.1, E = 48.5 ± 0.3 kcal) in good agreement with the original results under different experimental conditions. [b] This work.

but as the LPP experiments gave the same A factor but a slightly higher activation energy, we should increase the error limits for the latter. In the pyrolysis of II with excess butadiene there was no discrepancy between the LPP results for decomposition of II and the SFR results for the formation of methoxytrimethylsilane; either would be a good measure of the high-pressure limiting rate constant for reaction 9. The SFR experiments in the absence of butadiene gave almost the same Arrhenius parameters, indicating that the SFR conditions in themselves substantially reduced secondary reactions. Arrhenius parameters were lower and the rate constants for total decomposition higher in experiments without butadiene by LPP, indicating some occurrence of secondary reactions. A similar quite small effect of added butadiene was observed in the LPP experiments with III. Arrhenius parameters for the formation of propene and methoxytrimethylsilane from III in the SFR were equal within experimental error, confirming that reaction 7 was fast compared to reaction 6. These Arrhenius parameters are probably a good measure of k_6, notwithstanding the absence of butadiene, in view of the small effect that butadiene had in the SFR pyrolyses of II. In the pyrolysis of IV with added butadiene there is good internal agreement between the measurements in the SFR for the formation of methylsilane and 1-methylsilacyclopentene and between the LPP measurements for formation of the butadiene adduct and total decomposition of IV. For reasons discussed above, we marginally prefer the Arrhenius parameters derived from the SFR experiments for k_5.

In Table II our favored Arrhenius parameters and rate constants for the formation of dimethylsilylene from compounds I and II (reactions 8 and 9 are compared with those for formation of dimethylsilylene from hydrido- and chlorodisilanes (reactions 1, 10, 11). Before discussing trends in Table II, we note that the Arrhenius parameters for reaction 8 give $k_8 = 3 \times 10^{-5}$ s^{-1} at 222 °C, in quite remarkable agreement with the value of 4.7×10^{-5} s^{-1} obtained by Atwell et al.[4] under drastically different conditions in solution.

The values of $k_{350^\circ\mathrm{C}}$ in Table II show a substantial trend in the ease of formation of $\mathrm{Me_2Si{:}}$ from disilanes. Decomposition of $\mathrm{Me_3SiSiMe_2Cl}$ has a particularly low A factor, possibly because of complex formation,[8] but as all of the other A factors are approximately equal, the trend is mainly in the activation energy, E. We may illustrate the factors affecting E by applying Hess's Law to the decomposition of pentamethyldisilane, thus

$$\begin{array}{lr} \mathrm{Me_3SiSiMe_2H \rightarrow Me_3Si\dot{S}iMe_2 + H^\bullet} & \\ \mathrm{Me_3Si\dot{S}iMe_2 \rightarrow Me_3Si^\bullet + Me_2Si{:}} & \\ \mathrm{Me_3Si^\bullet + H^\bullet \rightarrow Me_3SiH} & \\ \hline \mathrm{Me_3SiSiMe_2H \rightarrow Me_3SiH + Me_2Si{:}} & (1) \end{array}$$

$$\therefore\ \Delta H_1 = D(\mathrm{Me_3Si{-}\dot{S}iMe_2}) - [\mathrm{D(Me_3Si{-}H) - D(Me_3SiSiMe_2{-}H)}]$$

This treatment may be generalized, replacing $D(\mathrm{Me_3Si{-}\dot{S}iMe_2})$ by $\mathrm{D({\equiv}Si{-}\dot{S}i{=})}$ and $[D(\mathrm{Me_3Si{-}H}) - D(\mathrm{Me_3SiSiMe_2{-}H})]$ by $\Delta D(\mathrm{{\equiv}Si{-}R})$, thus

$$\Delta H_n = D(\mathrm{{\equiv}Si{-}\dot{S}i{=}}) - \Delta D(\mathrm{{\equiv}Si{-}R})$$

hence

$$E_n = D(\mathrm{{\equiv}Si{-}\dot{S}i{=}}) - \Delta D(\mathrm{{\equiv}Si{-}R}) + E_{-n} \qquad \text{(i)}$$

where E_{-n} is the activation energy of the reverse reaction, insertion of $\mathrm{Me_2Si{:}}$ into a σ-bond. Equation i applies to all reactions in Table II. It is not possible to establish absolutely the relative importance of the terms in eq i, but some reasonable conclusions may be drawn. For the specific case of reaction 1, an estimate of $D(\mathrm{Me_3Si{-}\dot{S}iMe_2})$ may be obtained by subtracting the silylene stabilization energy from the "normal" Si-Si dissociation energy, $D(\mathrm{Me_3Si{-}SiMe_3})$. The most recent estimate[18] for the former is 32 kcal·mol^{-1}, while the latter has been measured[19] as 80.5 kcal·mol^{-1}; hence $D(\mathrm{Me_3Si{-}\dot{S}iMe_2}) \simeq 48.5$ kcal·mol^{-1}. This is close to the experimental value of E_1 in Table II, but we cannot infer that $E_{-1} \simeq 0$ because silyl substituents are known to be slightly bond weakening.[20] Hence, $[D(\mathrm{Me_3Si{-}H}) - D(\mathrm{Me_3SiSiMe_2{-}H})] > 0$, thus making $\Delta H_1 <$ 48.5 kcal.

For the pyrolysis of the three pentamethyldisilanes in Table II, $D(\mathrm{{\equiv}Si{-}\dot{S}i{=}})$ is identical in all three reactions (1), (9), and (10), while we would expect little variation in $\Delta D(\mathrm{{\equiv}Si{-}R})$ between these reactions; the effect of a silyl substituent on bond dissociation energies is small[20] and likely to be approximately constant.[21] Hence, $\Delta H_1 \simeq \Delta H_9 \simeq \Delta H_{10}$, and the observed differences in E for these reactions would arise largely from differences in E_{-n}, the latter being lowest for reaction −9, 2.9 ± 1.5 kcal higher for reaction −1, and 5.6 ± 1.5 kcal higher for reaction −10. It has been suggested from rather indirect evidence[22] that $E_{-11} \simeq 0$, but Ring and O'Neal[23] prefer ca. 2 kcal·mol^{-1}. The present results clearly confirm that $E_{-1} > 0$; if Ring and O'Neal's estimate for E_{-1} is approximately correct, then $E_{-9} \simeq 0$. The size of activation energies for silylene insertions is a highly topical question; some intriguing results are now being obtained from absolute rate measurements by kinetic spectroscopy.[24]

Comparing reactions 1 and 11, we expect $[-\Delta D(\mathrm{{\equiv}Si{-}R}) + E_{-n}]$ to be constant, but $D(\mathrm{{\equiv}Si{-}\dot{S}i{=}})$ to be ca. 2 kcal·mol^{-1} lower for (11) than for (1) because of the weakening effect on the Si-Si bond when methyl is re-

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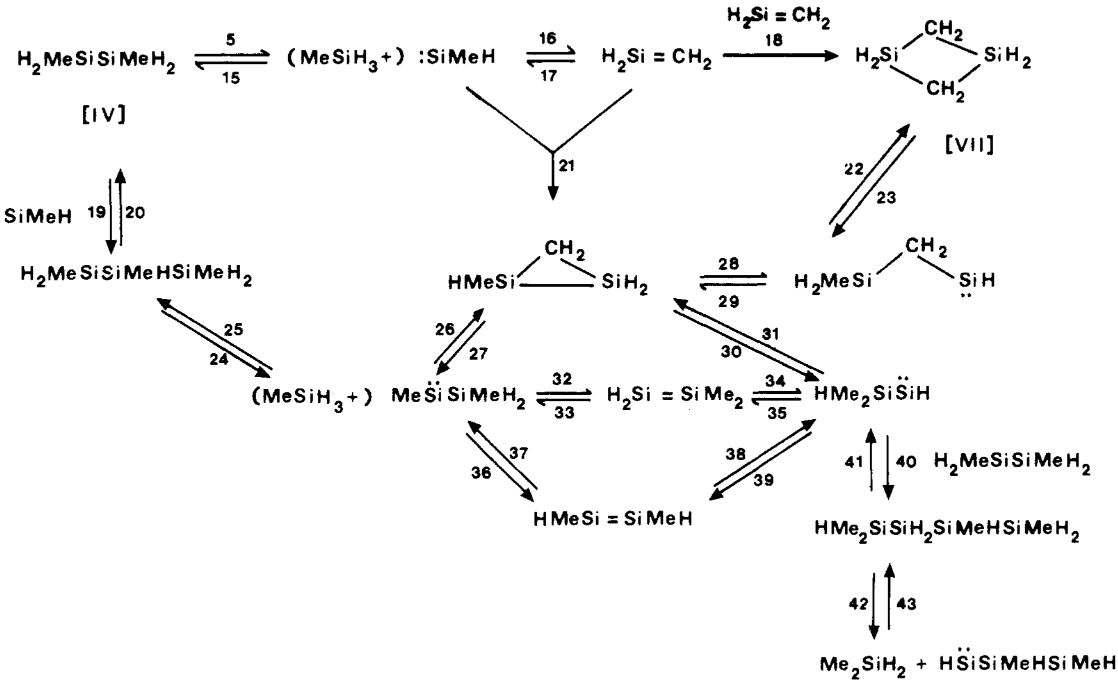
Table III. Arrhenius Parameters for Formation of Silylenes

reaction	log A	E/kcal	$k_{350°C}/s^{-1}$	ref
$H_2MeSiSiMeH_2 \xrightarrow{5} MeSiH_3 + :SiMeH$	14.3 ± 0.3	47.9 ± 0.6	3.1×10^{-3}	*a*
$H_2MeSiSiH_3 \xrightarrow{12} MeSiH_3 + :SiH_2$	15.3 ± 0.2	50.7 ± 0.4	3.1×10^{-3}	6
$H_2MeSiSiH_3 \xrightarrow{13} SiH_4 + :SiMeH$	14.1 ± 0.2	49.9 ± 0.4	4.3×10^{-4}	6
$H_2MeSiSiMe_2H \xrightarrow{14} Me_2SiH_2 + :SiMeH$	13.7 ± 0.6	46.2 ± 1.4	2.8×10^{-3}	7
$H_2MeSiSiMe_2H \xrightarrow{11} MeSiH_3 + :SiMe_2$	12.6 ± 2	46 ± 5	2.9×10^{-4}	7

[a] This work.

Scheme I. Partial Mechanism for Pyrolysis of IV



placed by hydrogen.[20] The results in Table II are consistent with that expectation, but there is a high uncertainty in E_{11} because reaction 11 was a minor pyrolysis pathway.[7]

In the two similar reactions (8) and (9), $\Delta D(\equiv Si—R)$ would be expected to be essentially constant, while E_{-8} and E_{-9} would be equal. The difference between E_8 and E_9 would arise mainly from the $D(\equiv Si—Si\equiv)$ term in eq i; i.e., replacing one methyl by methoxy appears to weaken the Si–Si bond by 5.5 ± 2 kcal·mol^{-1}. As this seems to be rather a large effect, it would be interesting to seek more direct evidence for it by bond dissociation energy measurements on methoxysilanes.

Our preferred results for IV are compared with earlier kinetic results for the pyrolysis of other disilanes involving formation of :SiMeH in Table III. Substituent effects in reactions 5, 13, and 14 are less pronounced than in the pyrolyses of disilanes with chlorine or methoxy substituents (Table II); all three activation energies lie within the range of 48 ± 2 kcal·mol^{-1}. The main point of interest in Table III is that while :SiMeH was produced in reactions 5, 13, and 14, only in the pyrolysis of IV was that process unique. In the pyrolysis of methyldisilane (V) and 1,1,2-trimethyldisilane (VI) there were concurrent processes forming other silylenes, reactions 12 and 11, respectively. Arrhenius parameters for these competing processes were deduced from the rates of formation of the appropriate monosilanes.[6,7] Unfortunately, our results from the pyrolysis of IV in the absence of butadiene call the validity of that procedure into question. Although Me_2SiH_2 was a minor product, only detected by us at the upper end of the temperature range and not reported at all previously,[14] it is significant mechanistically. The interconvertibility of silylenes, silenes, and disilenes offers almost limitless scope for mechanistic speculation in a pyrolysis of this complexity, but a relatively simple (but not unique) route to Me_2SiH_2 based on established precedents is given in Scheme I, where we suggest that the precursor to Me_2SiH_2 is the silylene $HMe_2Si\ddot{S}iH$, which interconverts with its isomer $Me\ddot{S}iSiMeH_2$ by 1,2-hydrogen and -methyl shifts from silicon to silicon involving disilene intermediates, as suggested by Boo and Gaspar,[25] and by 1,2-hydrogen shifts between silicon and carbon involving a disilacyclopropane intermediate.[11-13] The latter intermediate also links the pyrolysis of IV with that of 1,3-disiletane (VII), where Me_2SiH_2 was the main silicon-containing product after extensive pyrolysis.[13]

We have successfully applied computer modeling by numerical integration to simulate the results of a number of analogous pyrolyses,[11,26] including[27] Gaspar's methyl transpositions.[25] Our most recent efforts[27] have benefited from rules based on the principles of thermochemical kinetics[28] developed by O'Neal. Although these rules have not yet been published in full, their use is well-illustrated in a recent publication.[29] We have applied these methods and rules to a mechanism based on Scheme I, simply to see if such a mechanism could account for the observed temperature-dependent yield of Me_2SiH_2. The mechanism

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used for this modeling was much more extensive than Scheme I, which only includes those insertion and isomerization reactions directly relevant to the formation of $\mathrm{Me_2SiH_2}$, including a fuller range of these reactions raised the total number of reactions above 100.[30] Modeling this extended mechanism revealed that reactions in Scheme I could account satisfactorily for the observed formation of $\mathrm{Me_2SiH_2}$; $[\mathrm{Me_2SiH_2}]$:$[\mathrm{MeSiH_3}]$ was computed to be 0.11 at 453 °C and <0.01 at 382 °C. According to this particular model, the main route into the cycle interconverting $\mathrm{Me\ddot{S}iSiMeH_2}$ and $\mathrm{HMe_2Si\ddot{S}iH}$ in the pyrolysis of IV would be by reactions 19 and 24, not (21), the main reactions within the cycle being (32)–(39), involving the disilene intermediates rather than the disilacyclopropane. Consequently, VII was computed to be a very minor product, <1% $[\mathrm{MeSiH_3}]$, consistent with our failure to detect any VII in our experiments (VII would have been thermally stable[13] under these conditions).

Secondary reactions in the pyrolysis of V and VI would be even more extensive than those shown in Scheme I because in each case two different silylenes were formed in primary reactions, but if the rather tedious exercise of writing mechanisms analogous to Scheme I is undertaken, it shows that pyrolysis of VI would only be expected to give $\mathrm{Me_2SiH_2}$ and $\mathrm{MeSiH_3}$. However, some of the $\mathrm{Me_2SiH_2}$ would result from reactions of $:\mathrm{SiMe_2}$ and some of the $\mathrm{MeSiH_3}$ from reactions of :SiMeH. Likewise, in the pyrolysis of V, some $\mathrm{MeSiH_3}$ would be formed from :SiMeH and some $\mathrm{SiH_4}$ from $:\mathrm{SiH_2}$; we might also expect some formation of $\mathrm{Me_2SiH_2}$. As $\mathrm{Me_2SiH_2}$ was such a minor product in the pyrolysis of IV, the above complications in the pyrolysis of V and VI would likewise be minor; the relative importance of the primary pathways in these pyrolyses is probably much as given in Table III. Nevertheless, this work shows that some doubt must attach to the Arrhenius parameters for primary silylene-forming reactions in Table III that were obtained in the absence of a trapping agent to suppress secondary reactions.

The Arrhenius A factors in Tables II and III show some interesting features. Apart from reaction 10, where special factors may apply,[8] values of log *A* range from 12.6 to 12.9 for elimination of $:\mathrm{SiMe_2}$, from 13.7 to 14.3 for elimination of :SiMeH, and 15.3 for elimination of $:\mathrm{SiH_2}$ (log *A* was 14.5 for elimination of $:\mathrm{SiH_2}$ from $\mathrm{Si_2H_6}$).[31] As log *A* for this type of reaction would be expected[28] to be ca. 14.5–15, it appears that there is progressive loss of internal rotors in the transition state with increasing methyl substitution at the silicon that is eliminated as a silylene.

Experimental Section

All of the disilanes were generous gifts from Professor T. J. Barton of Iowa State University (compounds II and III), Professor R. Damrauer of the University of Colorado at Denver (compound I), and Professor E. Hengge of the Technical University of Graz (compound IV). Propene, methoxytrimethylsilane, and dimethoxydimethylsilane were obtained commercially and methylsilane and dimethylsilane were synthesized by lithium aluminum hydride reduction of the corresponding methylchlorosilanes, while 1-methylsilacyclopentene was synthesized by preparative-scale pyrolysis of IV with butadiene; 1,1-dimethylsilacyclopent-3-ene was a gift from Dr. G. Manuel of the University Paul Sabatier, Toulouse, France. As the adduct of :SiMeH to butadiene gave only one GC peak and as our reference sample was prepared pyrolytically, calibration for that product was straightforward. The procedure adopted for the corresponding adduct of $:\mathrm{SiMe_2}$, where two isomers were detected, was to measure the area of both GC peaks and to calibrate the resulting total area against 1,1-dimethylsilacyclopent-3-ene. This was a reasonable procedure because the latter was by far the major product, and the GC sensitivity to both isomers would be very similar.

Both the LPP and SFR apparatus used in this work were improved versions with data collection and analysis by dedicated microcomputers[32] and pressure measurement by MKS Baratrons.

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