The value of $k = 0.8$ required to achieve a satisfactory fit with experiment appears quite low for actinide compounds, and corresponds to values found for d transition metal compounds.[29] However, this value of $k$ can be interpreted to imply a strong interaction between the actinide ions and the COT orbitals, and is qualitatively consistent with the pronounced covalency inferred from the Mössbauer results of $Np(COT)_2$.

This interpretation of the magnetic susceptibility data is based on a much oversimplified model, which, however, does show the importance of covalent bonding for actinide(IV)–COT compounds and correctly predicts the diamagnetism of $Pu(COT)_2$. The temperature dependence of the diamagnetic susceptibility of $Pu(COT)_2$ is quite unusual, and no explanation for this phenomenon is apparent. Detailed studies on the optical and magnetic properties of these compounds remain to be done, and should provide experimental evidence for a more quantitative model.

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(28) J. D. Axe and G. Burns, *Phys. Rev.*, **152**, 331 (1966).

(29) M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 10 (1968).

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# Pyrolysis of Monosilane

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**Abstract:** The pyrolysis of silane–silane-$d_4$ mixtures and silane-$d_4$ in the presence of hydrogen has been examined. The results from these experiments and those reported by Purnell and Walsh[1] strongly suggest that silane decomposes by the following route: $SiH_4 \rightarrow SiH_3 + H$; $H + SiH_4 \rightarrow H_2 + SiH_3$; $SiH_3 + SiH_4 \rightarrow Si_2H_6 + H$; $2SiH_3 \rightarrow Si_2H_6$. With this result, the activation energy obtained by Purnell and Walsh can be used to demonstrate that $D_{298}°(SiH_3\text{–}SiH_3)$ and $D_{298}°(SiH_3\text{–}H)$ are of the order of 81 and 94 kcal mol$^{-1}$, respectively. Results from the pyrolysis of methylsilane–methylsilane-$d_3$ mixtures suggest that in addition to the reactions present in the silane decomposition, steps forming methylsilene and hydrogen are also important in the pyrolysis of methylsilane.

The pyrolysis of monosilane has been investigated by a number of workers.[2] A more recent kinetic study has been carried out by Purnell and Walsh.[1] They demonstrated that the pyrolysis of silane was homogeneous when carried out over a silicon mirror. Their results were most consistent with either mechanism A, molecular hydrogen elimination

$$SiH_4 \longrightarrow SiH_2 + H_2 \tag{1}$$

$$SiH_2 + SiH_4 \rightleftharpoons Si_2H_6 \tag{2}$$

$$SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8 \tag{3}$$

or mechanism B, H atom formation (free-radical chain)

$$\begin{array}{lll} SiH_4 \longrightarrow SiH_3 + H & \text{initiation} & (4) \\ H + SiH_4 \longrightarrow H_2 + SiH_3 & & (5) \\ & \text{chain} & \\ SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H & & (6) \\ 2SiH_3 \longrightarrow Si_2H_6 & \text{termination} & (7) \end{array}$$

Although it was not possible to determine which route was operative, they felt that a mechanism involving silene was most probable.

In this paper, we present our results, which, when combined with those of Purnell and Walsh,[1] allow for an analysis of the pyrolysis of monosilane.

## Experimental Section

All reactions were carried out in a Pyrex glass vacuum system. Separations were made by trap-to-trap distillations with the use of standard slush baths. Silane and silane-$d_4$ were prepared by the reduction of silicon tetrachloride with lithium aluminum hydride or deuteride. The silane-$d_4$ had present a small (~5%) amount of silane-$d_3$. Infrared spectra were obtained in 10-cm gas cells on a Perkin-Elmer Model 337 spectrophotometer, while mass spectra were obtained on a Hitachi Model RMU-6E mass spectrometer.

The static pyrolyses were carried out in a cylindrical vessel of 198-cm$^3$ volume whose walls were coated with a silicon mirror.[1] The temperature was measured with a thermometer inserted into a well in the reaction vessel which was inside an electric furnace. An equimolar silane–silane-$d_4$ mixture was expanded from a trap on the vacuum line into the heated reaction zone. After 10 sec, the pressure was noted and the stopcock between the trap and the reaction vessel was closed. After 2.5 min, the reaction mixture was returned to the vacuum system for analysis.

The pyrolysis of silane-$d_4$–hydrogen mixtures was carried out in the same manner from previously prepared silane-$d_4$–hydrogen mixtures.

The flow pyrolyses were carried out in a Vycor reaction tube previously described.[3] For these reactions, 1.08 mmol of an equimolar silane–silane-$d_4$ mixture was cycled with a Toepler pump through a silicon-mirrored heated tube (at 460°) and two traps cooled to −130°. The average pressure before the heated tube was 67 mm. A −112° bath was used in the pyrolysis of equimolar mixtures of methylsilane and methylsilane-$d_3$.

The silane fractions were analyzed from infrared spectra. The infrared spectrum[4] of $SiH_3D$, $SiH_2D_2$, or $SiHD_3$ each has a strong band which has zero overlap with bands from other silanes. Therefore, it was possible to obtain at least an approximate analysis of our silane mixtures. The disilane mixtures were analyzed from mass spectra of the disilane fractions. The mass spectrum of each disilane has been previously reported.[5] These analyses are most accurate for ratios of $Si_2D_6$:$HSi_2D_5$:$H_2Si_2D_4$:$H_3Si_2D_3$. The ratios of the more highly hydrogenated species are less reliable. The hydrogen mixture was also analyzed by mass spectra.

In a separate control experiment it was demonstrated that an $H_2$–$D_2$ mixture does not exchange H atoms over a silicon mirror under conditions used in our experiments.

## Results

The pyrolysis of equimolar silane–silane-$d_4$ mixtures was examined in a static system and in a circulating flow system with low-temperature (−130°) trapping

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(1) J. H. Purnell and R. Walsh, *Proc. Roy. Soc., Ser. A*, **293**, 543 (1966).

(2) T. R. Hogness, T. L. Wilson, and W. C. Johnson, *J. Amer. Chem. Soc.*, **58**, 108 (1936); see work of K. Stokland, discussed in ref 1.

(3) J. J. Kohanek, P. Estacio, and M. A. Ring, *Inorg. Chem.*, **8**, 2516 (1969).

(4) J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956); M. A. Ring and D. M. Ritter, *J. Amer. Chem. Soc.*, **83**, 802 (1961).

(5) M. A. Ring, G. D. Beverly, F. H. Koester, and R. P. Hollandsworth, *Inorg. Chem.*, **8**, 2033 (1969).

Table I. The Per Cent Composition of the Disilane and Hydrogen Fractions from the Decomposition of Equimolar $SiH_4$–$SiD_4$ Mixtures

| Mode | % decomposition | % disilanes $Si_2D_6$ | $HSi_2D_5$ | $H_2Si_2D_4$ | $H_3Si_2D_3$ | $D_2Si_2H_4$ | $DSi_2H_5$ | $Si_2H_6$ | % hydrogens $D_2$ | HD | $H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow pyrolysis | 4 | 17 | 12 | 17 | 0 | 16 | 6 | 32 | 28 | 31 | 41 |
| Static pyrolysis | 2 | 5 | 12 | 27 | 15 | 26 | 10 | 5 | 20 | 46 | 34 |
| Photolysis[a] | ~3 | 12 | 17 | 17 | 0 | 8 | 9 | 37 | 24 | 22 | 54 |
| Discharge[a,b] | ~3 | 10 | 5 | 21 | 0 | 8 | 12 | 44 | 18 | 29 | 53 |
| Discharge[a,c] | ~3 | 9 | 20 | 13 | 14 | 6 | 13 | 25 | 20 | 44 | 36 |

[a] Reference 5. [b] High pressure (0.30 atm). [c] Low pressure (0.014 atm).

Table II. Results of the Pyrolysis of $SiD_4$–$H_2$ Mixtures

| Time, min | Temp, °C | Total pressure, mm | Ratio $H_2/SiD_4$ | % composition of hydrogen $D_2$ | HD | $H_2$ |
|---|---|---|---|---|---|---|
| 135 | 380 | 383 | 1.20 | 41 | 43 | 16 |
| 10 | 380 | 279 | 2.43 | 12 | 43 | 45 |
| 5 | 310 | 230 | 3.32 | 0.7 | 2.8 | 96.5 |

Table III. Results of the Pyrolysis of Equimolar Mixtures of $CH_3SiH_3$ and $CH_3SiD_3$ (flow)

| Temp, °C | Pressure, mm | % decomposition | % composition of hydrogen $D_2$ | HD | $H_2$ |
|---|---|---|---|---|---|
| 515 | 10 | 4 | 28 | 21 | 51 |
| 510 | 15 | 4 | 32 | 16 | 52 |

of the product disilanes. In Table I, we list an average of the product ratios of the disilane and hydrogen fractions from flow pyrolyses at 460° and 67 mm, from the photolysis and electric discharge decompositions reported earlier,[5] and from a static (328° and 266 mm) pyrolysis which was typical of those examined between 290 and 375°.

The most significant difference in the results of the two pyrolyses occurred in the ratio, *R*, between the amount of mixed silanes ($SiH_{4-x}D_x$, with $x = 1$–$3$) formed and the amount of disilanes produced. In the static pyrolysis, 1.39 mmol of the silane mixture was pyrolyzed, yielding a 1.37-mmol mixture of silanes (containing about 0.3 mmol of mixed silanes) and 0.01 mmol of mixed disilanes. In the flow pyrolysis, 1.08 mmol was pyrolyzed, yielding a 1.02-mmol mixture of silanes (containing about 0.05 mmol of mixed silanes) and 0.02 mmol of mixed disilanes.

The results listed in Table II are from static pyrolyses of silane-$d_4$–hydrogen mixtures. In Table III we list our results from the pyrolyses of equimolar mixtures of methylsilane and methylsilane-$d_3$ in a flow system with low-temperature (−112°) trapping. The dimethyldisilane product fraction was not analyzed, since data were not available on these mixed dimethyldisilanes.

## Discussion

**A. Mechanism of the Pyrolysis of Monosilane. Mechanism A *vs.* Mechanism B.** In the flow pyrolyses of our equimolar $SiH_4$–$SiD_4$ mixtures, with low-temperature trapping of the product disilanes, only relatively small amounts of mixed silanes ($HSiD_3$, $H_2SiD_2$, $DSiH_3$) were formed. Therefore the HD, obtained in comparable yields to the $H_2$ and $D_2$ formed, must have been produced in primary reactions. This result favors mechanism B (free-radical chain process) over mechanism A (molecular hydrogen elimination). In fact, our data suggest that mechanism A is, at most, only of minor importance. For the reaction of silane-$d_4$ with hydrogen (Table II), we have the following from mechanism A

$$SiD_4 \longrightarrow SiD_2 + D_2 \tag{8}$$

$$SiD_2 + SiD_4 \longrightarrow Si_2D_6 \tag{9}$$

from mechanism B[6]

$$D + SiD_4 \longrightarrow D_2 + SiD_3 \tag{10}$$

$$D + H_2 \longrightarrow HD + H \tag{11}$$

$$H + SiD_4 \longrightarrow HD + SiD_3 \tag{12}$$

$$SiD_3 + SiD_4 \longrightarrow D + Si_2D_6 \tag{13}$$

If we momentarily ignore the $D_2$ produced in step 10, we have, from the last entry in Table II

$$\frac{d(Si_2D_6)/dt \text{ mechanism B}}{d(Si_2D_6)/dt \text{ mechanism A}} = \frac{\text{yield HD}}{2(\text{yield } D_2)} = 2$$

However, the above ratio should greatly exceed 2, since the rate of reaction 10 should be much greater than the rate of reaction 11,[7] and much of the $D_2$ produced would be expected to arise from the chain mechanism *via* reaction 10. The molecular mechanism (A) can therefore contribute at a *maximum* 33% to the overall decomposition, and from the above reasoning, it must contribute much less.

**B. Proposed Mechanism.** Any proposed mechanism (A or B) must explain the various disilanes formed, the change in the relative ratios of these disilanes formed in the static pyrolyses compared to the flow pyrolyses (see Table I), and the fact that the ratio, *R*, of the quantity of mixed silanes ($SiH_{4-x}D_x$, where $x = 1$–$3$) *vs.* the quantity of disilanes produced varied from about 30/1 in the static pyrolyses to about 2.5/1 in the flow pyrolyses. We feel that all of these results can be explained wholly on the basis of mechanism B with two additional processes: (1) hydrogen abstraction from silane by silyl radicals

$$SiH_3 + SiD_4 \longrightarrow SiH_3D + SiD_3 \tag{14}$$

and most important (2) the decomposition equilibrium of disilanes into silene and silane

$$Si_2H_6 \rightleftharpoons SiH_4 + SiH_2 \tag{15}$$

Reaction 14 provides a path for mixed silane production, while reaction 15 is a process by which both mixed silanes and disilanes can be formed. Reaction 14 should be operative in both the flow and static pyrolyses, while reaction 15 should be very important in the static pyrolysis but relatively unimportant in the flow pyrolysis. The latter follows from the fact that disilane products in the flow system were removed by trapping soon after their formation.

**C. Justification for Reactions 14 and 15.** Reaction 14 should be as fast and probably faster than reaction 6

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(6) For mechanism B we have calculated a chain length of $10^{11.5}$ (see Appendix), so that essentially all of the disilane is formed in step 6 (= step 13).

(7) $A_{10} \sim A_{11}$ and $E_{10} \leq E_{10}$, since $\Delta H_{10}° \simeq -10$ kcal mol$^{-1}$, while $\Delta H_{11}° \simeq 0$ kcal mol$^{-1}$.

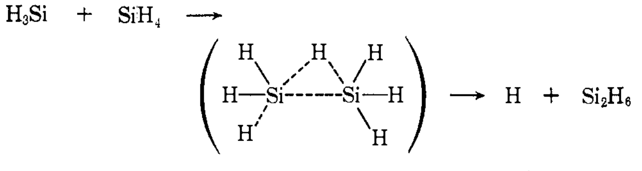
(formation of $Si_2H_6 + H$), since one would estimate that $E_{14} \leq E_6$ and $A_{14} \geq A_6$. It should be pointed out that reaction 14 is not essential to the explanation of our data.

Reaction 15 is a secondary reaction. Inclusion into the overall mechanism suggests that disilane decomposition into silene and silane is fast relative to the overall silane decomposition. The reverse of reaction 15 must also be extremely fast (see ref 12).

There are at present no reliable kinetic data on the pyrolysis of polysilanes, but our qualitative studies on the pyrolysis of disilane and trisilane[8] show that disilane is thermally more stable than trisilane.[9] The inference, by extrapolation then, is that silane should be more stable than disilane. Certainly by analogy with the hydrocarbons, such a stability sequence ($SiH_4 > Si_2H_6 > Si_3H_8$ in stability) is intuitively reasonable. A rough calculation from the data of Tebben and Ring[8] gave a rate of disilane decomposition an order of magnitude larger than the decomposition rate for silane observed by Purnell and Walsh.[1]

Another qualitative result is pertinent to this point. In the flow pyrolysis of $Si_2D_6$ in the presence of excess $CH_3SiH_3$,[10] the products observed were $SiD_4$ and $CH_3SiH_2SiD_2H$,[11,12] with only trace quantities of $D_2$ and no HD. At the end of this pyrolysis, silane-$d_4$ product pressures in the flow pyrolysis chamber were about the same as those of the disilane. Thus, from the small yields of $D_2$ and lack of HD formation it would appear that the product silane-$d_4$ was relatively stable compared to disilane-$d_6$.

**D. Disilane Product Formation.** With a long chain length operative in mechanism B,[6] the disilane must be formed in step 6. We propose that the activated complex for step 6 is



where the silyl radical electron attacks a d orbital. For the $SiH_4$–$SiD_4$ mixtures, the primary product disilanes obtained would therefore be $Si_2H_6$, 1,1-$D_2Si_2H_4$, 1,1-$H_2Si_2D_4$, and $Si_2D_6$. Decomposition of the primary product disilanes into a silene and silane (eq 15) would give $SiH_2$, $SiD_2$, HSiD, and mixed silanes. Insertion of HSiD into $SiH_4$ and $SiD_4$ (reverse reaction 15) would then give $HSi_2D_5$ and $DSi_2H_5$ as secondary product disilanes. The observed relative yields of disilanes in the flow pyrolyses where reaction 15 is suppressed coincide with this mode of production (*i.e.*, primary product disilane yields > secondary product disilane yields).

In the static pyrolyses, reaction 15 should be much more important; thus H–D mixing in the product disilanes should appear more statistical. This is as observed (see Table I).

**E. Mixed Silanes.** We propose that the mixed silanes ($SiH_{4-x}D_x$, where $x = 1$–$3$) were formed from reactions 14 and 15. Since reaction 15 becomes much more important in the static pyrolyses (see section D), the relative quantities of mixed silanes ($SiH_{4-x}D_x$, where $x = 1$–$3$) *vs.* total disilanes formed should be appreciably greater in the static pyrolysis than in the flow pyrolysis. This is as observed (see Table I).

**Energetics.** Our product study results point to mechanism B as the principle path operative in the pyrolysis of silane. Purnell and Walsh[1] favored mechanism A mainly as a result of energy considerations. It is necessary, therefore, to reevaluate the thermochemistry of the decomposition to see if the observed activation energy is really inconsistent with mechanism B. In addition, the *A* factor must be examined to see if it is "reasonable" with regard to the elementary reaction *A* factors and reaction rate theory. Although mechanism B cannot be proved, it is possible to show that it is consistent with most of the data, both qualitatively and quantitatively.

**A. The Activation Energy.** In terms of mechanism B[1]

$$k_{\text{exptl}} = 10^{15.2-55.9/\theta} \ (\text{l./mol})^{1/2}\,\text{sec}^{-1} \qquad (16)$$

$$E_{\text{exptl}} = 55.9 \text{ kcal/mol}^{-1} = E_6 + {}^1/_2E_4 \qquad (17)$$

$$E_6 = DH^\circ(\text{SiH}_3\text{–H}) - DH^\circ(\text{SiH}_3\text{–SiH}_3) + E_{-6} \qquad (18)$$

Purnell and Walsh have suggested that $E_{-6} \simeq E_5$. Gunning, *et al.*,[13] have calculated $E_5 \simeq 8.3$ kcal $mol^{-1}$, but have suggested that this activation energy may actually be lower by 2–3 kcal $mol^{-1}$. In disagreement with Purnell and Walsh, we feel that the H abstraction reaction (5) is not at all comparable to the addition–displacement reaction (−6), and view the latter to be a hydrogen atom (relatively strong Lewis base) attack on the relatively good Lewis acid, disilane. Such reactions generally have very low activation energies, and a value for $E_{-6}$ between 0 and 2 kcal $mol^{-1}$ does not seem unreasonable.

There is considerable uncertainty in the bond dissociation energies in silane and disilane (eq 18). If one equates average bond energies[14] in silane to the first bond dissociation energy, then $\overline{DH}^\circ(\text{SiH}_3\text{–H}) = 76.8$ kcal $mol^{-1}$ and $DH^\circ(\text{SiH}_3\text{–SiH}_3) = 46.9$ kcal $mol^{-1}$. These values are quite inconsistent with the observed activation energy in the silane decomposition, since by assigning $E_{-6} = 0$ kcal $mol^{-1}$ (its minimum value), one obtains from eq 18 and 19 $E_{\text{decomposition SiH}_4} \geq 68.3$ kcal $mol^{-1}$, a value at least 12 kcal $mol^{-1}$ higher than observed.

Electron impact studies by Steele and Stone[15] have given $DH^\circ(\text{SiH}_3\text{–H}) = 94 \pm 3$ kcal $mol^{-1}$ and also $DH^\circ(\text{SiH}_3\text{–SiH}_3) = 81 \pm 4$ kcal $mol^{-1}$. These values *are* consistent with mechanism B *and* with the accepted heats of formation of silane ($\Delta H_f^\circ(SiH_4) = 7.3$ kcal $mol^{-1}$) and of disilane ($\Delta H_f^\circ(Si_2H_6) = 17.1$ kcal $mol^{-1}$).[14] If we assume that the heats of formation are good to about ±1.5 kcal $mol^{-1}$ (which seems quite realistic), then the disilane electron impact bond dissociation energy gives $\Delta H_f^\circ(SiH_3) = 49 \pm 3$

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[8] E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969).

[9] Under similar conditions, disilane decomposition was first noted at 370°, while trisilane decomposition was first noted at 340°.

[10] P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, **9**, 1068 (1970).

[11] Trapped out at −95°.

[12] This product arises from an $SiD_2$ insertion into $CH_3SiH_3$. These products (without HD formation) strongly suggest that disilane decomposes into silane and silene (eq 15).

[13] M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87**, 179 (1965).

[14] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

[15] W. C. Steele and F. G. A. Stone, *J. Amer. Chem. Soc.*, **84**, 3599 (1962); W. C. Steele, L. D. Nichols, and F. G. A. Stone, *ibid.*, **84**, 441 (1962).

kcal mol$^{-1}$. Saalfeld and Svec[16] have also obtained bond dissociation energies from electron impact studies. Their results give (in kcal mol$^{-1}$)

$$DH°(SiH_3\text{–}H) = 95.2$$

$$DH°(SiH_3\text{–}SiH_3) = 84$$

$$\Delta H_f°(SiH_3) = 50.4$$

Equations 17 and 18 can be combined and written in terms of radical and molecule heats of formation; thus

$$E_{\text{exptl}} = {}^3/_2[\Delta H_f°(H) - \Delta H_f°(SiH_4)] - {}^1/_2\Delta H_f°(SiH_3) + \Delta H_f°(Si_2H_6) + E_{-6} \quad (19)$$

Using average values from the electron impact data[15,16] we have, from eq 19

$$55.9 \pm 0.5 = {}^3/_2[52.1 - 7.3 \pm 1.5] - {}^1/_2(49.7 \pm 3) + 17.1 \pm 1.5 + E_{-6} \quad (20)$$

$$55.9 \pm 0.5 = 59.1 \pm 5.4 + E_{-6} \qquad \text{kcal mol}^{-1} \quad (21)$$

A very similar result was obtained by Purnell and Walsh.[1] We see that $E_{-6}$ can be as high as 2.7 kcal mol$^{-1}$ and still fit the data. In fact, $E_{-6}$, could even be higher for two reasons. First, Purnell and Walsh observed a homogeneous unit gas effect (*i.e.*, an acceleration of the reaction rate with added inert gases), and concluded that this could only arise from a first-order reaction in its falloff region. In mechanism B, this reaction would have to be reaction 4; therefore, $E_{4(p\rightarrow\infty)}$ would be higher than experimentally observed.[17] In addition, a more realistic estimate of the activation energy error[18] gives $\Delta E \simeq 1.2$ kcal mol$^{-1}$. Thus, $E_{-6}$ could be as high as 6.1 kcal mol$^{-1}$ and still be consistent with the observed activation energy, the electron impact bond dissociation energies, and the silane and disilane heats of formation.

**B. The Frequency Factor.** With regard to the observed $A$ factor, mechanism B is in some difficulty, although not irreparably so. We have $\log A_{\text{exptl}} = {}^1/_2(\log A_4 - \log A_7) + \log A_6 = 15.1$. Assuming unit collision efficiency for reaction −6 and $\sigma = 4A°$, one obtains $A_{-6(\max)} \simeq 10^{12}$ l./(mol sec). The entropy change for reaction 6 can be estimated to be[19] $\Delta S_{6,-6} \simeq -9 \pm 1$ eu; therefore, the maximum value for $A_6$ is about $10^{10}$ l./(mol sec). This requires that $A_4/A_7 \simeq 10^{10}$ mol/l. Since it is difficult to see how the unimolecular decomposition $A_4$ can be much larger than $A_4 \leq 10^{16}$ sec$^{-1}$,[19] one must accept a radical–radical termination $A$ factor of $A_7 \simeq 10^6$ l./(mol sec). This seems unreasonably low when compared to alkyl radical recombination rate constants, which are in most cases within a factor of 10 of collision frequencies[20] (*e.g.*, $A = 10^{10.3}$ l./(mol sec) for $CH_3 + CH_3$). We have seen how arguments by analogy with hydrocarbon behaviors lead to errors in silane chemistry. It is perhaps equally unwarranted to make $A$ factor identifications, the silyl radical being another species altogether. We conclude, therefore, that since other evidence for mechanism B is strong, the silyl–silyl radical termination reactions must be unusually slow.[21]

**Photolysis and Electric Discharge.** Results obtained from the photolysis[5] at 1470 Å (195 kcal mol$^{-1}$) and the electric discharge decomposition[5] of equimolar silane–silane-$d_4$ mixtures are listed in Table I. We proposed[5] that the main primary process in the photolysis was step 1. The formation of $HSi_2D_5$, $DSi_2H_5$, and HD was explained on the basis of decomposition of "hot" molecules owing to the high energies required for photochemical interaction. The fact that the ratio of $HSi_2D_5/Si_2D_6$ is greater in the photolysis than in the flow pyrolysis, while the ratio $HD/D_2$ or $HD/H_2$ is less in the photolysis than in the flow pyrolysis does suggest that mechanism A is important in the photolysis. However, since it is now clear that mechanism B does not require $H_3SiSiD_3$ to be present in the disilane product fraction (as was thought earlier[5]), the initial decomposition of silane into silyl radicals and a hydrogen atom, or even into silene radicals and two hydrogen atoms, cannot be ruled out. In fact, it is easier to explain all of the HD formed by including some hydrogen atom producing reaction.

The results from the high-pressure discharge data when analyzed as above seem to suggest that hydrogen atoms are formed in the initial decomposition along with either silyl or silene radicals. The low-pressure results can still be explained by higher energies and/or less collisional stabilization of energetic molecules.[5]

**Pyrolysis of Methylsilane.** The major products from the pyrolysis of methylsilane are hydrogen and 1,2-dimethyldisilane.[3] This result could arise from a mechanism similar to routes A or B. An examination of the results presented in Table III compared to those in Table I leads us to suggest that both mechanisms A and B are of comparable importance. This would be the case if step 6 is relatively slower in comparison to the other steps in the methylsilane decomposition as compared to the silane decomposition. The chain length in mechanism B would thus be shorter in the methylsilane decomposition than in the silane decomposition.

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## Appendix

Calculation of chain length for mechanism B (eq 4–7) at 328° is as follows.

$$\text{Chain length} = \frac{\text{rate of disilane production}}{\text{rate of initiation (eq 4)}}$$

$$= \frac{\left(\dfrac{k_4}{k_7}\right)^{1/2} k_6[SiH_4]^{3/2}}{k_4[SiH_4]}$$

$$\cong \frac{10^{15-56/\theta}[SiH_4]^{1/2}}{10^{16.0-94/\theta}}$$

$$\cong 10^{13.0}(3 \times 10^{-3})^{1/2}$$

$$\cong 10^{11.5}$$

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[16] F. E. Saalfeld and H. J. Svec, *J. Phys. Chem.*, **70**, 1753 (1966).

[17] A maximum increase of about $(s - {}^3/_2)RT \simeq 2.7$ kcal mol$^{-1}$ can be estimated, where $s$ is the effective number of classical oscillators contributing energy with the reaction coordinate and is roughly given by $(\bar{C}_v/R) - 3$ at $\bar{T}_{\text{mean}}$.

[18] S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 93.

[19] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 65.

[20] S. W. Benson and H. E. O'Neal, "National Standard Reference Data Series," National Bureau of Standards Circular 21, U. S. Government Printing Office, Washington, D. C., 1970, p 36.

[21] Note that reactions 4 and 7 must also be in their falloff regions if the inert gas effect observed by Purnell and Walsh is correct. This only serves to compound the $A$ factor problem, since it would tend to lower $A_4$ more than $A_7$.