tively, variations in the solvent may be changing the nature of the encounter which could in turn yield different probabilities for the catalyzed deactivation, energy transfer, and electron transfer processes.

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Relative Insertion Rates of Silylene and Evidence for Silylsilylene Insertion into Silicon–Hydrogen and Silicon–Silicon Bonds

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Abstract: The relative rates of SiH_2 insertions into several methylsilanes and methylgermane in competition with disilane were measured in our recirculating flow system. When the results are expressed in terms of relative rate per E–H (E = Si, Ge) bond available for insertion, the order was as follows: $(CH_3)_3SiH > Si_2H_6 > (CH_3)_2SiH_2 > CH_3SiH_3 > SiH_4 > CH_3GeH_3$. No insertion products were found with CH_3PH_2 or $ClSiH_3$ in competition with disilane. The above rates have been explained in terms of the hydridic character of the E–H bond. Trisilane was pyrolyzed at 330° and the primary products were SiH_4, SiH_2, Si_2H_6, and Si_2H_4. The diradicals, SiH_2 and Si_2H_4, have been chemically trapped by $(CH_3)_3SiD$ and Si_3H_8, and the structure of Si_2H_4 is discussed. The relative ratios of normal to isotetrasilane and normal to isopentasilane produced from the neat pyrolysis of Si_3H_8 provide the strongest evidence to date for SiH_2 and Si_2H_4 insertions into both silicon–hydrogen and silicon–silicon bonds.

Although the chemistry of divalent carbon has been exhaustively investigated and reviewed,[1] studies with divalent silicon have been concentrated mainly on SiF_2[2] and other disubstituted silylenes.[3] Silylene, the silicon analog of methylene, has recently been shown to be an intermediate in the homogeneous thermal decomposition of disilane.[4,5] The insertion of SiH_2

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \tag{1}$$

into silicon–hydrogen bonds has been conclusively demonstrated[4,5] and insertion into silicon–silicon bonds has been suggested to account for product ratios in the static pyrolysis of Si_2H_6 (n-Si_4H_{10}/i-$Si_4H_{10} \simeq 4.8$)[5] and the higher per bond insertion into Si_2H_6 compared with SiH_4.[6]

Qualitative results from the SiH_2 insertions into $(CH_3)_2SiH_2$ and $ClSiH_3$[4] suggested that silylene acts as an electrophile during insertions into silicon–hydrogen bonds and that substituents do significantly affect the insertion rates into the remaining Si–H bonds. In an effort to better understand these nonstatistical insertion rates, we have investigated the relative insertion rates of SiH_2 into various silanes, CH_3GeH_3, and CH_3PH_2 in competition with Si_2H_6. Particular attention has been paid to the change in relative insertion rates per Si–H bond of silane due to the successive replacement of hydrogen atoms by methyl groups.

An investigation of the primary products in the pyrolysis of Si_3H_8 has produced evidence for (i) a new diradical species, Si_2H_4, which has been chemically trapped and (ii) the insertions of SiH_2 and Si_2H_4 into silicon–silicon bonds.

Results and Discussion

The pyrolysis of silicon hydrides lead to the formation of slightly more stable lighter hydrides and to more catenated less stable hydrides.[7] Therefore, only initial rates of a static silicon hydride decomposition are valid. An alternate approach to avoid secondary decompositions is to carry out the pyrolysis in a flow system containing a low-temperature trap which removes the less volatile (and less stable) products from the reaction stream. Further, the decompositions should be carried out for a very short time so that the partial pressure of any lighter product is still low. The problem of secondary reactions can occur in studying reactions of SiH_2 generated from Si_2H_6. Silane is the other product from the Si_2H_6 decomposition and it

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[2] J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971).

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[5] M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

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must be kept at low partial pressures. Therefore, our SiH_2 insertion reactions were carried out at low conversions to avoid SiH_4 buildup and subsequent formation and reactions of SiH_3 radicals from the decomposition of SiH_4.[8]

In our earlier study of Si_3H_8 we obtained both Si_2H_6 and SiH_4[7] and suggested that the SiH_4 was not a result of secondary Si_2H_6 decomposition. In the present study, we have reexamined the Si_3H_8 decomposition at much lower per cent decomposition to avoid the possibility of SiH_4 formation from product Si_2H_6.

A. Insertion Reactions of SiH_2. The results listed in Table I were obtained from the flow pyrolysis of Si_2H_6 at 350° in the presence of a second SiH_2 trapping agent. A low-temperature U trap was present to remove the insertion products from the stream. Our present results and that from the competitive reaction of $^{31}SiH_2$ with Si_2H_6 and SiH_4[6] can best be compared on a per-bond basis as reported in the Table I.

Table I. Relative Insertion Rate of SiH_2 at 350° (per E–H bond)

Expt no.	Trapping agent	Insertion product	Rel insertion rate
1	Si_2H_6	Si_3H_8	1.0
2	$(CH_3)_3SiH$	1,1,1-$(CH_3)_3Si_2H_3$	1.6 ± 0.2
3	$(CH_3)_2SiH_2$	1,1-$(CH_3)_2Si_2H_4$	0.7 ± 0.1
4	CH_3SiH_3	$CH_3Si_2H_5$	0.4 ± 0.05
5	SiH_4	Si_2H_6	0.3 ± 0.1[a]
6	CH_3GeH_3	$CH_3GeH_2SiH_3$	0.2 ± 0.05[b] 0.02
7	CH_3PH_2	CH_3PHSiH_3[c]	<0.01[c]
8	$ClSiH_3$	$ClSi_2H_5$[c]	<0.01[c]

[a] From fast-neutron irradiation of phosphine–silane–disilane mixtures, ref 6. [b] See text. [c] Insertion product not observed.

The results listed in Table I assume that the insertion products did not decompose before they were removed by the cold trap. It is interesting to note the much higher relative per-bond insertion rate into CH_3SiH_3 (1.4 compared to Si_2H_6 at 1.0) obtained from the static copyrolysis of Si_2H_6 with CH_3SiH_3.[9] Bowrey and Purnell have noted that in their static pyrolysis of Si_2H_6[9] "*the lack of balance between monosilane and trisilane and the finding of a finite yield of tetrasilanes at zero time almost certainly reflects the speed of secondary reactions and the inadequacy of the simple extrapolation procedure employed.*" Since Si_3H_8[7] is less stable than $CH_3Si_2H_5$[10] the product ratio, $Si_3H_8/CH_3Si_2H_5$, from the Si_2H_6–CH_3SiH_3 static pyrolysis will be only a lower limit. Thus the per-bond insertion rate into CH_3SiH_3 will be an upper limit. The following discussion demonstrates that in our flow system, secondary reactions did not occur except only to a very slight extent in experiment 6.

The copyrolysis of a Si_2H_6–Si_2D_6 mixture would produce Si_3H_8, $SiH_3SiH_2SiD_2H$, $SiD_3SiD_2SiH_2D$, and Si_3D_8. The decomposition of these trisilanes would produce SiH_4, SiD_4, and SiD_2H_2 (see part B). The copyrolysis of an equimolar Si_2H_6–Si_2D_6 mixture did not produce SiH_2D_2 under our reaction conditions which demonstrates that Si_3H_8 produced in our pyrolyses did not decompose but was quantitatively removed by our cold "U" traps. The products from the flow pyrolysis of Si_2D_6 in the presence of CH_3SiH_3 were SiD_4 and $CH_3SiH_2SiD_2H$ at 375°.[4] Since $CH_3Si_2H_5$ decomposes by 1,2-hydrogen shifts into CH_3SiH_3, SiH_2, SiH_4, and CH_3SiH,[10] the decomposition of any $CH_3SiH_2SiD_2H$ would have generated SiH_2D_2. The absence of this product from the pyrolysis of Si_2D_6 with CH_3SiH_3 demonstrated that the $CH_3SiH_2SiD_2H$ produced was quantitatively removed by the "U" traps. The very similar thermal stabilities observed for Si_2H_6, $CH_3Si_2H_5$, and 1,2-$(CH_3)_2Si_2H_4$[4,10] imply that the 1,1-$(CH_3)_2Si_2H_4$ and 1,1,1-$(CH_3)_3Si_2H_3$ formed were also quantitatively removed in our system. The pyrolyses of Si_2D_6 in the presence of $ClSiH_3$ and CH_3PH_2 did not produce SiH_2D_2. If SiD_2 had inserted into $ClSiH_3$ and CH_3PH_2 the expected products would be $ClSiH_2SiD_2H$ and CH_3PHSiD_2H. The compound 1,1-$Cl_2Si_2H_4$ and SiH_3PH_2 both decompose by 1,2-hydrogen shifts to yield SiH_4 as one of the products.[11] Thus it is reasonable to expect that $ClSiH_2SiD_2H$ and CH_3PHSiD_2H would also decompose to produce SiH_2D_2. The absence of this silane demonstrates that the silylene insertion products with $ClSiH_3$ and CH_3PH_2 did not form and then decompose.

The last control experiment was carried out by the pyrolysis of Si_2D_6 and CH_3GeH_3. The SiH_2 insertion product into CH_3GeH_3 was isolated and identified to be $CH_3GeH_2SiH_3$. The SiD_2 insertion product (assumed to be $CH_3GeH_2SiD_2H$) was pyrolyzed at 360° and produced SiH_2D_2. The control pyrolysis of Si_2D_6 and CH_3GeH_3 at 350° did produce a small quantity of SiH_2D_2 as part of the monosilane fraction. Therefore, the $CH_3GeH_2SiH_3$ produced in our competitive reaction (results for Table I) did decompose to a slight extent in the thermal zone. For this reason, the relative insertion rate reported for CH_3GeH_3 (experiment 6 Table I) is listed as 0.2 ± (0.05, 0.02).

The data listed in Table I can be best correlated with the negative charge on the hydrogen under attack. The rates of halogenation of silanes with AgCl are in the order $CH_3SiH_3 > SiH_4 > ClSiH_3$,[12] while a similar order was found for halogenation with PF_5:[13] $(CH_3)_3SiH > CH_3SiH_3 > Cl_3SiH$. These data suggest that the methyl group has an opposite inductive effect (electron donating) from chlorine when bonded to silicon. This conclusion is consistent with the silicon–hydrogen stretching frequencies which increase with chlorination and decrease with methylation for mono- and disilanes.[14] This is expected from the changes in s and p character for the silicon orbitals bonded to hydrogen.[15] Thus, based on silicon–hydrogen stretching frequencies, the order of hydridic character is[14] $(CH_3)_3SiH > (CH_3)_2SiH_2 > Si_2H_6 > CH_3SiH_3 > SiH_4 > ClSiH_3$. A similar correlation can also be made for GeH_2 insertion into Ge–H bonds.[16] For the mono-

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silanes examined (experiments 2–5 and 8) the observed order correlates exactly with hydridic character. The insertion rate for Si_2H_6 is higher than expected on the basis of hydridic character of the silicon–hydrogen bond. We contend that the apparent increased silylene affinity of Si_2H_6 is due to insertions into the silicon–silicon bond (the product is indistinguishable from the silicon–hydrogen bond insertion product) and will offer evidence in the following sections that SiH_2 appears to insert into the silicon–silicon bond of Si_3H_8.

The lower relative insertion rate of SiH_2 into CH_3GeH_3 compared with CH_3SiH_3 is consistent with a decrease in hydridity of the nonmetal hydrogen bond. This effect is very pronounced in CH_3PH_2 where the hydrogen probably has a positive charge.

B. Initial Decomposition Modes in Si_3H_8. The pyrolysis of Si_3H_8 has been examined at 330° in a recirculating flow system with a −63° trap. Gas chromatographic analysis demonstrated that after 0.2% decomposition SiH_4 and Si_2H_6 had been produced in a ratio of 2.4 ± 0.3. The final Si_2H_6 partial pressures were less than 0.01 mm (calcd) while the Si_3H_8 partial pressures were about 1–2 mm. Under these conditions, essentially all of SiH_4 formed must have come from the decomposition of Si_3H_8 owing to the greater thermal stability of Si_2H_6 compared with Si_3H_8[7] and with the much greater partial pressures of Si_3H_8 compared with Si_2H_6 in the thermal zone. These products could be produced by a 1,2-hydrogen shift as observed in Si_2H_6[4,5] or by silicon–silicon bond rupture to produce

$$Si_3H_8 \xrightarrow{k_2} HSiSiH_3 + SiH_4 \qquad (2)$$

$$Si_3H_8 \xrightarrow{k_3} SiH_2 + Si_2H_6 \qquad (3)$$

SiH_3 and Si_2H_5 radicals followed by hydrogen atom

$$Si_3H_8 \longrightarrow SiH_3 + Si_2H_5 \qquad (4)$$

$$SiH_3 + Si_3H_8 \longrightarrow SiH_4 + Si_2H_5 \qquad (5)$$

$$Si_2H_5 + Si_3H_8 \longrightarrow Si_2H_6 + Si_3H_7 \qquad (6)$$

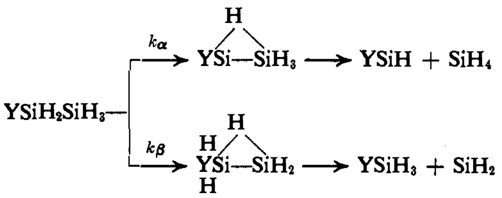
abstractions to yield SiH_4 and Si_2H_6. The fact that the copyrolysis of Si_3H_8 in the presence of excess CH_3SiD_3 produced SiH_4 and no SiH_3D eliminates the presence of abstraction reactions like eq 5 and 6. Therefore, our results are only consistent with an initial Si_3H_8 decomposition proceeding *via* eq 2 and 3 in a ratio of about 2:1. This conclusion is further supported by the chemical trapping of $HSiSiH_3$ and SiH_2 described later in this report.

Statistically, the ratio, k_2/k_3, should be 0.67.[17] In $CH_3Si_2H_5$, the ratio, k_7/k_8, should be 0.67 (statistically) and was found to be 0.57 ± 0.03.[10]

$$CH_3SiH_2SiH_3 \xrightarrow{k_7} SiH_4 + CH_3SiH \qquad (7)$$

$$CH_3SiH_2SiH_3 \xrightarrow{k_8} CH_3SiH_3 + SiH_2 \qquad (8)$$

These results and the relative thermal stabilities of Si_3H_8, $CH_3Si_2H_5$, and Si_2H_6 can be explained with the use of the following substituted disilane activated complexes where Si_3H_8 can be represented as a SiH_3 substituted disilane provided the reaction modes are doubled as demanded by space symmetry. The rate constant for a 1,2-hydrogen shift *from* the substituted silicon (the central silicon in Si_3H_8) is defined as k_α and the rate constant for the shift *to* the substituted silicon is k_β.



Experimentally, the normalized ratios k_α'/k_β' ($k_i' = k_i$/number of effective hydrogens) were 0.86 (0.57/0.67) when Y was CH_3 and 3.6 (2.4/0.67) when Y was SiH_3. These results and the decreased thermal stability of Si_3H_8 and $CH_3Si_2H_5$ can be rationalized by separating the concerted decomposition into a heterolytic silicon–silicon bond rupture and a hydride transfer step in addition to steric factors. During heterolytic cleavage, the bonded electron pair should be drawn to the most acidic leaving group. In Si_3H_8 the greater Lewis acidity of the Si_2H_5 group[12,18–20] would favor formation of $\ddot{Si}HSiH_3$ instead of $\ddot{Si}H_2$. In $CH_3Si_2H_5$, one would expect the SiH_3 group to be a slightly stronger Lewis acid than the CH_3SiH_2 group which would favor k_β'. Hydride transfer is favored by greater hydridic character of the transferring hydrogen and increased Lewis acidity of the silicon acceptor. The relative acidities ($Si_2H_5 > SiH_3$; $SiH_3 > CH_3SiH_2$) would favor k_β' in Si_3H_8 and k_α' in $CH_3Si_2H_5$; however, the hydride character of the transfer H atom would favor k_α' in both Si_3H_8 and $CH_3Si_2H_5$.[21]

In addition, steric factors would favor k_α' in both Si_3H_6 and $CH_3Si_2H_5$. These effects have been summarized in Table II. The most important factor appears to be the leaving group acidity and its effect on silicon–silicon rupture. The decreased thermal stability of Si_3H_8 compared with Si_2H_6 or $CH_3Si_2H_5$ can be explained by an increase in k_α due to the disilanyl group.

Table II. Favored Process in Substituted Disilane Decompositions

Compound	k_α'/k_β'	Leaving group acidity	H transfer/		Steric
			acidity	hydridity	
Si_3H_8	3.6	k_α'	k_β'	k_α'	k_α'
$CH_3Si_2H_5$	0.86	k_β'	k_α'	k_α'	k_α'

C. Insertion Reactions of $HSiSiH_3$ and SiH_2 into Si-Si Bonds. The neat pyrolysis of Si_3H_8 was carried out at 330° in a recirculating flow systems with a −63° trap. The heavy products were a Si_4H_{10} mixture and a Si_5H_{12} mixture in a ratio of 1/1.4, respectively. The tetrasilanes were produced by SiH_2 insertion into Si_3H_8. The pentasilanes could have been formed by a SiH_2 insertion into a product tetrasilane or by reaction of a Si_2H_4 species with Si_3H_8. We can rule out any

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[17] In Si_3H_8, the six terminal hydrogens can transfer one way while the two central hydrogens can transfer two ways so k_2/k_3 is 0.67 and not 0.33.

[18] C. H. Vandyke and A. G. MacDiarmid, *Inorg. Chem.*, 3, 747 (1964).

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[21] The hydridic character[14] of the hydrogens follows the order $Si_2H_6 > SiH_4$, $CH_3SiH_3 > SiH_4$. We assume this same order holds for the groups $Si_2H_5 > SiH_3$, $CH_3SiH_2 > SiH_3$.

significant SiH_2 insertion into a product tetrasilane since the gas-phase ratio, Si_3H_8/Si_4H_{10}, reached an estimated minimum of 75/1 at the end of the experiment. An additional argument against a second SiH_2 insertion is that in similar experiments with Si_2H_6 in the same and similar systems we never detected a second SiH_2 insertion product. Therefore we can conclude that the pentasilanes were produced by the reaction of Si_2H_4 with Si_3H_8.

The species Si_2H_4 could be SiH_3SiH, $H_2Si{-}SiH_2$, or $H_2Si{=}SiH_2$. At the present time none of these structures can be established unambiguously, but the authors favor the structure H_3SiSiH for reasons noted below.[22,23] The flow pyrolysis of Si_3H_8 at 370° in the presence of a 10/1 gas phase excess of $(CH_3)_3SiD$ yielded $(CH_3)_3Si_2H_2D$, Si_4H_{10}, $(CH_3)_3Si_3H_4D$, and Si_5H_{12}. These results are consistent with SiH_2 and SiH_3SiH insertions.

Prior evidence does exist for a silysilylene insertion into an Si–H bond. The major product from the reaction of Si atoms with $(CH_3)_3SiH$ was $(CH_3)_3SiSiH_2Si(CH_3)_3$.[24] This result is consistent with Si atom insertion to produce $(CH_3)_3SiSiH$ followed by insertion into the Si–H bond in $(CH_3)_3SiH$.

In the neat pyrolysis of Si_3H_8 approximately 35% of the SiH_3SiH presumed formed from the decomposition of Si_3H_8 inserted to produce the pentasilanes with the remainder polymerizing within a few centimeters of the thermal zone. This is much lower than the nearly quantitative insertions for SiH_2[4] and $HSiCH_3$[10] but much greater than that for $HCCH_3$ which yields C_2H_4 almost quantitatively in competition with solution insertion into $C_6H_5SiH_3$.[25] The difference in chemistry observed for $HSiSiH_3$ and $HCCH_3$ again demonstrates the low probability of forming silicon–silicon double bonds.

The ratio of the product isomers were determined by glpc to be n-/i-Si_4H_{10} = 3.7 and n-/i-Si_5H_2 = 2.1. Absolute calibration by glpc was not possible due to the small quantities of these isomers which were available only as reaction products. Extrapolation of an empirical relationship between relative retention times and thermal conductivity response (see Experimental Section) for the lower silanes appears justified. Even a large error (±25%) in interpreting these product ratios would not alter the very significant difference between the tetra and penta isomer distribution or the conclusions based thereon.

One would expect $HSiSiH_3$ insertions into the central silicon–hydrogen bond of Si_3H_8 relative to the terminal hydrogens to be as or less favorable than SiH_2 insertions into these same bonds. On this basis, if one assumes that only silicon–hydrogen bond insertions occur, one would expect $n\text{-}/i\text{-}Si_5H_{12} \geq n\text{-}/i\text{-}Si_4H_{10}$. On the contrary, the very significant increase in i-Si_5H_{12} product can best be explained by silicon–silicon bond insertions. The insertion of SiH_2 into the six terminal silicon–hydrogen bonds of Si_3H_8 and both silicon–silicon bonds yields n-Si_4H_{10} while insertion into only the two central silicon–hydrogen bonds yields i-Si_4H_{10}. With $HSiSiH_3$, however, insertion into the six terminal hydrogen bonds form n-Si_5H_{12} while insertions into the two silicon–silicon and both central silicon–hydrogen bonds produce i-Si_5H_{12}. Thus, while silicon–silicon bond insertions of SiH_2 increase the n- to i-isomer ratio, these same insertions by $HSiSiH_3$ decrease the n- to i-isomer ratio. Our results are consistent with both SiH_2 and SiH_3SiH insertions into silicon–silicon bonds although definitive experiments have consistently eluded these authors as well as other investigators. It should be noted that silicon–silicon bond insertions into Si_2H_6 can account for its apparent increased silylene affinity in comparison with the methylsilanes.

Experimental Section

Reagents. Disilane, methylsilanes, and CH_3GeH_3 were prepared by the reduction of the corresponding chlorides with $LiAlH_4$ or $LiAlD_4$. Trisilane was prepared by the pyrolysis of Si_2H_6.[7] Methylphosphine and chlorosilane were prepared as described in the literature.[26] The reagents were purified by trap to trap distillations and were identified by infrared and mass spectra. The purity of these compounds was checked by demonstrating that infrared bands and mass spectral peaks of logical impurities were absent from spectra of these compounds. As an example, for Si_2H_6, the strong 910-cm^{-1} band of SiH_4 and strong 717- and 705-cm^{-1} bands of Si_3H_8 were absent from the infrared spectrum. The mass spectrum contained peaks due only to the ions $Si_2H_{6-x}^+$ (m/e 64–56) and SiH_{3-x}^+ (m/e 33–28).

Instrumental Procedure. Infrared spectra were recorded on a Perkin-Elmer 337 or 621 spectrometer while mass spectra were obtained on a Hitachi Perkin-Elmer RMU-Ge spectrometer. The nuclear magnetic resonance spectrum of $CH_3GeH_2SiH_3$ was taken on a Varian A-60 with computer averaging techniques. The hydrides were separated and analyzed on a 5 m × 6 mm column containing 20% squalene on 60–80 mesh Aeropac 30.[27] The trisilane pyrolysis was analyzed on a 1 m × 6 mm column of 20–40 mesh 5 Å molecular sieve and/or a 2 m × 6 mm column containing 20% tricresyl phosphate on 60–80 mesh Aeropac 30. The detector used was a thermal conductivity cell (Loenco D-202-L-8, 8–10 K ohm) operated at reduced filament current to prevent pyrolysis of the hydrides. The detector circuit was interfaced to a Varian 620/i computer programmed to integrate peak areas. The gas chromatograph was connected to a trapping unit for collecting up to five separate fractions. Each collecting trap consisted of a U trap containing 5 cm of Aeropac 30 coated with 10% squalene and maintained at −196°. The helium carrier gas, dried by passage over 5 Å molecular sieve, could by-pass the collected unit to allow removal or reintroduction of the samples. The columns and detector were operated at room temperature. Chromatography of hydrides has been described in detail by Phillips and Timms.[28]

General Procedure. The pyrolyses were carried out in a recirculating flow system consisting of a Toepler pump, thermal zone, and "U" trap. The thermal zone was a 10 cm × 10 mm o.d. Pyrex tube heated by means of a high-temperature tape (available from Brisco Manufacturing Co., Columbus, Ohio) and insulated with magnesia insulation. Temperatures were measured by means of a thermometer inserted in a Pyrex well between the heating tape and the thermal zone. The temperature was regulated by a constant voltage power supply. The Pyrex thermal zone was coated with a silicon mirror from silane decompositions to ensure homogeneity.[9]

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[22] Although no positive evidence for the structure H_3SiSiH exists, rather strong arguments against the other two structures can be made. (i) For $H_2Si{=}SiH_2$, one notes that no real evidence for $p_\pi{-}p_\pi$ bonds involving silicon atoms exists, and the authors believe that such a species if it were to exist, would not react readily with Si_3H_8. (ii) The biradical structure, $H_2\dot{S}i{-}\dot{S}iH_2$ can be eliminated by thermodynamic considerations. The equilibium for the conversion of SiH_3 radical to SiH_4 and SiH_2 lies completely toward SiH_4 and SiH_2.[23] The biradical, $H_2\dot{S}i{-}$

$$2SiH_3 \rightleftharpoons SiH_4 + SiH_2 \quad (K_{327^\circ} = 10^{15.9})$$

SiH_2, can be invisioned as two silyl radicals held in close proximity by a silicon–silicon bond. The conversion of this species to SiH_3SiH must be very rapid compared to any bimolecular process.

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The reagents were condensed into the flow system with the U trap at −196° and isolated from the vacuum line by a stopcock. The reaction was started by replacing the liquid nitrogen with a slush bath which served to set the partial pressure of the reagents and to remove the heavy products from the reagent stream. The gas-phase ratio of reagents was determined by gas chromatography or mass spectrometry of aliquots taken with the Toepler pump at the top and bottom of its cycle. Sufficiently large amounts of reagents were used to ensure nearly constant partial pressure throughout the reaction. The pyrolysis was terminated by cooling the U trap to −196° and closing the stopcocks to the thermal zone to prevent further pyrolysis. The reaction mixture was reintroduced into the vacuum line and most of the reagents were recovered from the reactants by trap to trap distillation. The reagent fraction was shown to contain no products by mass spectrometry. The remainder of the reagents and products were analyzed by gas chromatography.

Analysis. Authentic samples of the reaction products were prepared by pyrolysis of disilane and the appropriate trapping agent as indicated in Table I. The infrared spectra of $CH_3Si_2H_5$,[29] 1,1-$(CH_3)_2Si_2H_4$,[30] and 1,1,1-$(CH_3)_3Si_2H_3$[31] were identical with those reported in the literature. Higher molecular weight impurities were shown to be absent by mass spectrometry while vapor pressures and the absence of infrared bands due to less volatile starting materials eliminated lower molecular weight impurities. The authentic product samples and reagents were used to determine retention times and weight correction factors. A good correlation between the square root of the relative retention time and the weight correction factor was obtained for the lower silicon hydrides and digermane. The standard error of estimate for the least-squares fit of Si_2H_6, $(CH_3)_3SiH$, $CH_3Si_2H_5$, Ge_2H_6, and Si_3H_8 was 0.02. The weight correction factors for compounds which were not available in sufficient quantities for direct measurement were estimated from this least-squares graph.

1. Competitive Reactions with Si_2H_6 at 350°. The following data represent average results of at least three identical reactions.

A. $(CH_3)_3SiH$. Disilane (0.49 mmol) and $(CH_3)_3SiH$ (1.47 mmol) were pyrolyzed for 4 hr with a −78° cold trap. The product fraction condensed at −112° was chromatographed yielding a product ratio, $Si_3H_8/(CH_3)_3Si_2H_3$ of 4.35 from a gas-phase ratio of $Si_2H_6/(CH_3)_3SiH$ of 1.10.

B. $(CH_3)_2SiH_2$. A mixture of 0.98 mmol of each of Si_2H_6 and $(CH_3)_2SiH_2$ (gas-phase ratio of 0.78, respectively) was pyrolyzed for 8 hr with a −95° trapping bath. The product fraction condensed at −112° had a Si_3H_8/1,1-$(CH_3)_2Si_2H_4$ ratio of 3.56.

C. CH_3SiH_3. Disilane and CH_3SiH_3 (0.50 mmol each) were pyrolyzed for 4 hr with a −95° trap. The gas-phase ratio, Si_2H_6/CH_3SiH_3, was 0.11. The product fraction condensed at −119° had a ratio of $Si_3H_8/CH_3Si_2H_5$ of 0.54.

In a separate experiment to demonstrate the reliability of the methods used, 1.50 mmol of Si_2H_6 and 0.30 mmol of CH_3SiH_3 were pyrolyzed under similar conditions. The product ratio decreased to 0.30 while the gas-phase ratio increased to 0.63. These results yield a per bond relative insertion rate of 0.37 compared with 0.4 for the experiments from the equimolar reactions.

D. $ClSiH_3$. Disilane (0.86 mmol) and $ClSiH_3$ (0.94 mmol) were pyrolyzed for 4 hr with a −95° trapping bath. The infrared spectra of the fraction condensed at −112° contained only those bands reported for Si_3H_8[32] while the very strong bands of $ClSi_2H_5$[33] at 814, 801, and 547 cm^{-1} were missing. Mass spectral analysis of this fraction showed no evidence of $ClSiH_x^+$ or $ClSi_2H_x^+$ fragment ions. The $ClSiH_3$ was recovered unaltered.

E. CH_3PH_2. Disilane and CH_3PH_2 (1.34 mmol each) were pyrolyzed for 8 hr with a −78° trapping bath. Although CH_3PH_2 was in slight excess in the gas phase, the infrared spectra of the fractions condensed at −112° contained no absorption band due to phosphorus–hydrogen bonds (2400–2300 cm^{-1}). The chromatogram of this fraction contained only one peak corresponding to Si_3H_8. The fraction passing −112° contained only SiH_4, Si_2H_6, and CH_3PH_2.

F. CH_3GeH_3. Disilane (0.30 mmol) and CH_3GeH_3 (1.49 mmol) were pyrolyzed for 8 hr with a −95° trapping bath which set the gas-phase ratio (Si_2H_6/CH_3GeH_3) at 0.08. The fraction condensed at −112° contained $Si_3H_8/CH_3GeH_2SiH_3$ = 0.77. In addition, trace amounts of other methylgermanes were observed due to the very slow decomposition of CH_3GeH_3.[34] Separate control experiments in which the Si_2H_6/CH_3GeH_3 gas-phase ratio was greatly altered (*i.e.*, extent of CH_3GeH_3 decomposition was varied) demonstrated that CH_3GeH_3 decomposition did not change the $Si_3H_8/CH_3GeH_2SiH_3$ product distribution.

2. Control Reactions with Si_2D_6. A. Si_2H_6. The pyrolysis of an equimolar Si_2H_6–Si_2D_6 mixture (0.51 mmol each) at 360° for 3 hr with a −78° bath produced a 0.09 mmol silane fraction whose infrared spectrum demonstrated that less than 5% SiH_2D_2[35] (743 and 944 cm^{-1}) was present. When this experiment was repeated at 350° no SiD_2H_2 was produced.

B. $ClSiH_3$. The 360° pyrolysis of 0.36 mmol of Si_2D_6 and 0.22 mmol of $ClSiH_3$ was carried out for 3 hr with a −78° trapping bath. The infrared spectrum of the fraction passing −160° (0.07 mmol) was that of SiD_4[35] (681 cm^{-1}) and a trace of SiD_3H[35] (851 cm^{-1}). Absorptions due to SiD_2H_2 were absent as were those of $SiDH_3$[36] (781 and 908 cm^{-1}) and SiH_4. Further, the infrared spectrum $ClSiH_3$ was unchanged after the reaction.

C. CH_3PH_2. Disilane-d_6 (0.38 mmol) and CH_3PH_2 (0.36 mmol) were pyrolyzed at 360° for 3.5 hr with a −78° trapping bath. The product fraction passing −160° (0.05 mmol) was shown to be free of SiD_2H_2 as described in section A. The spectrum of the entire final sample contained absorptions due only to the starting reagents.

D. CH_3GeH_3. A 360° pyrolysis of Si_2D_2 (0.42 mmol) and CH_3GeH_3 (0.50 mmol) for 4.5 hr with a −78° trapping bath produced 0.08 mmol of silane. The infrared spectrum indicated that this fraction was about 10% SiD_2H_2 and about 90% SiD_4. The product fraction condensed at −112° (0.07 mmol) was pyrolyzed further at 360° for 0.25 hr without a trapping bath. The products of this pyrolysis were primarily SiD_2H_2 and a methylgermane containing germanium–hydrogen and germanium–deuterium bonds identified by an infrared spectrum. A trace of SiD_4 (from Si_3D_8) was also produced. A 350°, 5 hr pyrolysis of Si_2D_8 (0.50 mmol) and CH_3GeH_3 (0.52 mmol) with a −95° cold trap produced a silane fraction containing less than 5% SiD_2H_2.

3. Identification of $CH_3GeH_2SiH_3$. The methylgermylsilane prepared in experiment 6 (Table I) was identified as follows. (i) The gas-phase infrared spectrum consisted of the following absorptions (cm^{-1}): 2970 (w), 2158 (vs), 2056 (vs), 1260 (m), 925 (m), 887 (s), 820 (vs), and 685 (m). The silicon–hydrogen stretching frequency (2158) was more intense than the germanium hydrogen stretch frequency (2056). (ii) The mass spectrum consisted of peaks due to the following heavy atom skeletons (envelope intensities): $CGeSi^+$ (61), GeSi (43), and Ge^+ (100). These data suggest that the product had the formula $CGeSiH_6$ and was most likely $CH_3GeH_2SiH_3$. (iii) The proton nmr spectrum (Table III) in $DCCl_3$ with TMS as an internal standard consisted of a CH_3 triplet and a –GeH_2SiH_3 multiplet of relative integrated intensity of 3:4.5 (calcd 3:5). It is obvious from the data listed in Table IV that our product was not $CH_3SiH_2GeH_3$ or $GeH_3CH_2SiH_3$ and therefore was $CH_3GeH_2SiH_3$.

Table III. Proton Nmr Spectra of Silagermaalkanes

Compound	τ (C–H)	τ (Si–H)	τ (Ge–H)	J_{HSiCH}, Hz	J_{HGeCH}, Hz
$CH_3GeH_2SiH_3$[a]	9.68	6.72[b]			4.0
$CH_3SiH_2GeH_3$[c]	9.71	6.17	7.03	4.8	
$GeH_3CH_2SiH_3$[c]	10.01	6.29	6.37	4.5	4.0

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4. Pyrolysis of Si_3H_6. A. Neat Pyrolysis. Trisilane aliquots (0.22 mmol) were pyrolyzed at 330° for short times with the cold bath at −63°. The entire samples were analyzed by chromatography. The results are listed in Table IV.

B. Neat Pyrolysis (Insertion Products). Trisilane (0.90 mmol)

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Table IV. Trisilane Pyrolyses at 330°

Time, hr	$(SiH_4/Si_3H_8)10^4$	$(Si_2H_6/Si_3H_8)10^4$	SiH_4/Si_2H_6
0.5	10	4.2	2.4
1.0	21	7.5	2.8
1.5	21	10	2.1

was pyrolyzed at 330° with the low-temperature trap set at −63° for 5.5 hr consuming 0.53 mmol of Si_3H_8. The products which passed the −57° trap and condensed at −78° were identified as a mixture of *n*- and *i*-S_4H_{10} (0.10 mmol) by its infrared spectrum and retention times.[37] Similarly the fraction which passed the −23° trap and condensed at −57° was a mixture of *n*- and *i*-Si_5H_{12} (0.07 mmol).[37] The ratio, *n*-Si_4H_{10}/*i*-Si_4H_{10}, was 2.2. In a similar experiment the ratios were 3.5 and 2.0.

C. Copyrolysis of Si_3H_8 and $(CH_3)_3SiD$. Trimethylsilane-*d* (1.42 mmol) and Si_3H_8 (0.45 mmol) were pyrolyzed at 370° for 5 hr with a −57° trapping bath. A mass spectrum of the fraction condensed at −78° (0.05 mmol) consisted of fragment ion envelopes of m/e = 101–105, 112–122, 129–137, and 147–152 which is consistent with the products $(CH_3)_3Si_2H_2D$, Si_4H_{10}, $(CH_3)_3Si_3H_4D$, and Si_5H_{12}, respectively.

D. Copyrolysis of Si_3H_8 with CH_3SiD_3. A mixture of Si_3H_8 (0.47 mmol) and CH_3SiD_3 (1.25 mmol) was pyrolyzed at 340° for 6 hr with a −63° trapping bath. The infrared spectrum of the fraction passing a −160° trap demonstrated that the SiH_4 produced was free from any SiH_3D as well as other deuteriosilanes.

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[37] The identification of the normal and iso isomers was based on the fact that the iso isomers have shorter retention times than the normal isomers. Further, the normal isomers were removable from the system by 5 Å molecular sieves.[28]

The Hammett Acidity Function for Some Superacid Systems. II.[1] The Systems H_2SO_4–HSO_3F, KSO_3F–HSO_3F, HSO_3F–SO_3, HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–SbF_5–SO_3

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Abstract: Using a set of aromatic nitro compound indicators, the Hammett acidity function, H_0, has been determined for the systems H_2SO_4–HSO_3F, KSO_3F–HSO_3F, HSO_3F–SO_3, HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–SbF_5–SO_3.

In part I[1] of this series we presented the results of our measurements of the Hammett acidity function, H_0, for the systems H_2SO_4–$H_2S_2O_7$, H_2SO_4–HSO_3F, H_2SO_4–HSO_3Cl, and H_2SO_4–$HB(HSO_4)_4$. This work provided for the first time quantitative, or at least semiquantitative, information on the relative acidities of these superacid systems. In recent years fluorosulfuric acid has become a widely used superacid solvent, and systems such as HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3 have become recognized as the most highly acidic media available. A 1:1 mixture of HSO_3F and SbF_5 has proved to be so useful as a medium for obtaining stable solutions of otherwise very unstable carbonium ions that it has been called "magic acid." The object of the work reported in this paper was to extend our earlier studies to these still more acidic superacid media based on fluorosulfuric acid and to obtain values for the Hammett acidity function for the systems HSO_3F–SO_3, HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–SbF_5–SO_3. During the course of the work it was necessary to make some measurements on the system HSO_3F–KSO_3F and to further study the HSO_3F–H_2SO_4 system in the region of excess HSO_3F; these results are also reported here.

Results and Discussion

Determination of H_0 Values. The indicators used in the present study were *p*-nitrochlorobenzene, *m*-nitrochlorobenzene, 2,4-dinitrotoluene, 2,4-dinitrofluorobenzene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, and 2,4,6-trinitrochlorobenzene. The ionization ratios, $I = [BH^+]/[B]$, of the indicators were determined by the spectroscopic method previously described[1] making use of the equation $[BH^+]/[B] = (\xi_B - \xi)/(\xi - \xi_{BH^+})$, where ξ is the measured extinction coefficient and ξ_B and ξ_{BH^+} are the extinction coefficients, at the same wavelengths (usually the wavelength of maximum absorption of BH^+) of the neutral, B, and protonated, BH^+, forms of the indicator, respectively. During the course of the work it became apparent that the polynitro indicators could undergo a second protonation at very high acidities. Use was made of this second protonation in the determination of the acidities for which no sufficiently weak neutral base was available.

As a result of his earlier studies of the protonation of nitro compounds in acid media Brand, *et al.*,[2] had concluded that the absorptions due to separate nitro groups are essentially independent and the diprotona-

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