RADIATION CHEMISTRY AND MASS SPECTROMETRY OF

VOLATILE SILANES AND GERMANES

Progress Report

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Preface

Our continuing study of the high-energy radiation chemistry of silane and germane systems may, as in the past, be subdivided into three types of investigation as follows:

- A. Gamma-ray radiolyses of silanes and germanes and of mixtures of these substances with organic compounds, free-radical scavengers and ion scavengers.
- B. Studies of the ion-molecule reactions occurring when systems corresponding to those of (A) are subjected to ionization by electron impact. This type of investigation affords an examination of the purely ionic component of a chemical conversion initiated by ionizing radiation.
- C. Studies of the free-radical reactions characteristic of gamma-ray radiolyses of systems corresponding to those of (A). Initiation of reaction in these investigations is by photo-sensitization so that ionization of the systems does not occur and we may study the pertinent free-radical reactions independently of the ionic processes.

In a program such as this one it is necessary to shift emphasis from time-to-time between chemical systems and between types of investigation, depending upon personnel, equipment, and directions suggested by the results obtained. This annual progress report describes work done from June 1, 1975 to August 31, 1976. During the report year most work was done with volatile silane and organo-silane systems and while the emphasis was almost equally divided between A, B, and C above, most progress was made in areas B and C. This report consists of abstracts of progress made in the various topics studied during the report-year.

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1. THE HYDROGEN-ATOM INITIATED DECOMPOSITION OF MONOSILANE

A mass-spectrometric study of the hydrogen-atom initiated decomposition of monosilane has been carried out. Silyl radicals were generated by mercury photosensitization of hydrogen-mono-silane mixtures which consisted of about 95% hydrogen. Under these conditions more than 94% of the $\text{Hg}(^3\text{P}_1)$ atoms that are quenched by collision react with hydrogen to form hydrogen atoms and all the hydrogen atoms formed react with monosilane via (1) to form silyl radicals.^{1,2} Our attention is centered on the further reactions of the silyl radicals.

The reactions were carried out in a photolysis cell containing a pin-hole leak leading into the ionization region of a time-of-flight mass spectrometer. In the photolysis of such a flow system the concentrations of all substances will approach steady-states that are reached when the rates of introduction into the cell become equal to rates of loss from the cell.

Illumination of the photolysis cell containing the H_2 - SiH_4 mixture with 2537 Å radiation results mainly in the formation of Si_2H_6 and depletion of SiH_4 . Small amounts of Si_3H_8 and Si_4H_{10} appear after long illumination times. In addition to the volatile products a solid film is deposited on the walls and quartz window of the cell.

In Figure 1 is shown the time dependence of the concentrations of SiH_4 and Si_2H_6 (both relative to the initial concentration of SiH_4) for two cells, one with a pyrex wall and one with a stainless

steel wall. For irradiation times greater than 50 seconds the behavior in the two cells is different. However, the initial slopes of both the depletion of SiH_4 and the formation of Si_2H_6 are independent of the cell wall. When the stainless steel cell was packed with quartz wool, identical results for the initial slopes were obtained. A fourth cell prepared by presilanation of the pyrex wall with $(\text{CH}_3)_2\text{SiCl}_2$ gave completely different results; the depletion rate of SiH_4 was reduced by a factor of 2, while the formation rate of Si_2H_6 was decreased by a factor of 7.

These data indicates that in a clean cell with walls which do not contain adsorbed silanes, the initial rates of depletion of SiH_4 and formation of Si_2H_6 are independent of the nature and area of the surface. The ratio of the initial rate of depletion of SiH_4 to the initial rate of formation of Si_2H_6 is 2 as the simple stoichiometry of (2) requires.

When the cell walls are silanated, most of the SiH_4 consumed does not produce Si_2H_6 or any other volatile product but results in an increased formation of film on the walls of the cell.

The protium-deuterium isotopic composition of the disilane formed by the $\text{Hg}(^3\text{P}_1)$ photosensitized reaction in a (96:2:2) H_2 - SiH_4 - SiD_4 mixture has been studied. The method used was to determine the mass spectra of the 56-68 region at a series of ionizing electron energies near the ionization potential of Si_2H_6 . Ion-currents of all parent ions and of m/e 60 relative to the ion current at m/e 68 were plotted as a function of nominal electron

energy. A linear extrapolation of the i_{60}/i_{68} ratio yields a nominal electron energy of 11.0 eV for the disappearance of all fragment ions from the spectrum. The relative amounts of the various deuterated disilanes are given by extrapolating each of the plots in Figure 2 to 11.0 eV and making isotope corrections. These results are shown below.

^{28}Si -Mass Spectrum of Disilane Products at 11 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>
62	Si_2H_6^+	90±26
63	$\text{Si}_2\text{H}_5\text{D}^+$	43±11
64	$\text{Si}_2\text{H}_4\text{D}_2^+$	37±15
65	$\text{Si}_2\text{H}_3\text{D}_3^+$	3±13
66	$\text{Si}_2\text{H}_2\text{D}_4^+$	100±16
67	Si_2HD_5^+	66±11
68	Si_2D_6^+	74±16

It is clear that $\text{Si}_2\text{H}_3\text{D}_3$ is virtually absent. This is in agreement with the proposal of Strausz et al.³ that association of silyl radicals does not occur and that the formation of disilane occurs by the sequence (3) and (4). The distribution of disilanes suggests that the H-atom attacks SiH_4 to form SiH_3 radicals about twice as

fast as it attacks SiD_4 to form SiD_3 radicals. This is in accord with the corresponding rate constant ratio of 2-2.5 as reported by Potzinger et al.⁴

Figure 1. Depletion of SiH_4 and formation of Si_2H_6 during photolysis.

Figure 2. Ion current ratios versus nominal electron energy.

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2. ION-MOLECULE REACTIONS IN $\text{SiH}_4\text{-D}_2$ MIXTURES.

The ion-molecule reactions characteristic of $\text{SiH}_4\text{-D}_2$ mixtures have been identified and the reaction cross-sections measured as functions of relative kinetic energy. The exothermic and thermoneutral reactions along with the respective enthalpy changes and cross-sections at 1 eV relative kinetic energy are shown in Table I. The endothermic reactions along with threshold energies and maximum reaction cross-sections are shown in Table II.

Table I.
Exothermic and Thermoneutral Ion-Molecule Reactions
in $\text{SiH}_4\text{-D}_2$ Mixtures

Reaction No.	Reaction	ΔH° (eV)	$\sigma(\text{\AA}^2)^{a,b}$
4	$\text{D}_2^+ + \text{SiH}_4 \rightarrow \text{Si}^+ + \text{D}_2 + 2\text{H}_2$	-2.9	2
5	$\rightarrow \text{SiH}^+ + \text{D}_2 + \text{H}_2 + \text{H}$	-2.0	2
6	$\rightarrow \text{SiH}_2^+ + \text{D}_2 + \text{H}_2$	-3.6	11
7	$\rightarrow \text{SiH}_3^+ + \text{D}_2 + \text{H}$	-3.2	34
8	$\rightarrow \text{D}_2\text{H}^+ + \text{SiH}_3$	-2.3	1
9	$\text{D}_3^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{D}_2 + \text{HD}$	-1.5	34
10	$\text{SiH}^+ + \text{D}_2 \rightarrow \text{SiD}^+ + \text{HD}$	~ 0	1.7
11	$\text{SiH}_2^+ + \text{D}_2 \rightarrow \text{SiHD}^+ + \text{HD}$	~ 0	0.5
12	$\rightarrow \text{SiD}_2^+ + \text{H}_2$	~ 0	0.2
13	$\text{SiH}_3^+ + \text{D}_2 \rightarrow \text{SiH}_2\text{D}^+ + \text{HD}$	~ 0	0.07

^a At 1 eV center-of-mass.

^b Estimated uncertainty of $\pm 40\%$.

D_2^+ reacts with SiH_4 to yield SiH_3^+ , SiH_2^+ , SiH^+ and Si^+ by exothermic processes that proceed with total cross-section near the Langevin orbiting value¹. D_3^+ reacts with SiH_4 to form only SiH_3^+ with a cross-section also near the Langevin value. The absence of SiH_2D^+ in this latter reaction suggests that SiH_3^+ is formed by direct hydride-ion transfer from SiH_4 rather than by the intermediate formation of SiH_4D^+ .

Table II

Endothermic Ion-Molecule Reactions in SiH_4 - D_2 Mixtures

Reaction No.	Reaction	Threshold Energy (eV)	$\sigma_{max}^{\circ} (A)^2$
14	$Si^+(^2P) + D_2 \rightarrow SiD^+ + D$	0.90 ± 0.10	$2.3 (3.2 \text{ eV})$
15	$(SiH^+)^* + D_2 \rightarrow SiHD^+ + D$	0.2 ± 0.05	$1.2 (1.5 \text{ eV})$
16	$\rightarrow SiD_2^+ + H$	-	$0.5 (2.7 \text{ eV})$
17	$SiH_2^+ + D_2 \rightarrow SiH_2D^+ + D$	0.38 ± 0.02	$0.55 (2.5 \text{ eV})$
18	$\rightarrow SiHD_2^+ + H$	~ 0.4	$0.015 (1.6 \text{ eV})$
19	$SiH_3^+ + D_2 \rightarrow SiH^+ + H_2 + D_2$	1.1^a	-

^a Calculated from thermochemical data.

All chemical reactions of Si-containing ions in their ground states with D_2 are endothermic. Energy thresholds for the D-atom pick-up reactions of Si^+ and SiH_2^+ yield thermochemical results in satisfactory agreement with values obtained by other methods.² SiH_3^+ reacts with D_2 solely to form SiH_2D^+ , a result indicating that only HD is eliminated from the $SiH_3D_2^+$ intermediate. This finding shows

the non-equivalence of D and H in the silanium ion formed by the association of SiH_3^+ with D_2 .

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3. EXTENSIVE REDISTRIBUTION OF FLUORINE AND HYDROGEN IN THE REACTION OF CF_3^+ WITH SiH_4 .

When CF_3^+ ions with relative kinetic energies in the range of 1-10 eV collide with SiH_4 the product-ion mass spectra (corrected for ^{29}Si and ^{30}Si isotopes) are as shown in Table I. At all three relative kinetic energies the predominant product ion is SiH_3^+ . On the basis of available thermochemical data¹⁻³ the only electrically neutral product that is energetically feasible at 1.3 eV is CF_3H and hence the predominant reaction must be written as in (1).

As the kinetic energy of the reactants is increased there is an enhanced formation of other products, including those such as SiH_2^+ , SiH^+ , CH_2^+ , CH^+ , and C^+ , all of which are formed in endothermic processes.

The fact that (1) is the major reaction in CF_3^+ - SiH_4 collisions is not surprising since it is well documented that the major reaction of silanes with positive ions is hydride transfer.⁴⁻⁷ Furthermore, kinematic studies of the H^- -transfer from silanes have shown that the reaction proceeds mainly by a direct stripping-type mechanism⁸ as contrasted to the formation of a long-lived intermediate complex.⁹ The surprising feature of the reaction is that at low kinetic energies ions such as CH_3^+ , CH_2F^+ and SiHF_2^+ , which represent extensive redistribution of H and F atoms, are formed.

This latter feature is surprising because at the pressures used, the mean free path in the collision cell is ~ 30 times longer than the

ion path and, hence, all products must result from a single collision of CF_3^+ and SiH_4 . Thus to form CH_3^+ for which only the neutral products SiHF_3 (or $\text{SiF}_2 + \text{HF}$) are energetically possible, a collision complex must be formed which holds together long enough for six (or seven) bonds to be broken and six bonds to be formed. In view of the tendencies of positive carbon centers to abstract hydride from silanes⁴⁻⁷ and of positive silicon centers to abstract fluoride from fluorocarbons,¹⁰ and on the basis of the known bridging properties of hydrogen and fluorine in inorganic¹¹ and organosilicon¹² chemistry, we propose the mechanism shown in Figure 1. In this mechanism the essential long-lived complex is held together by alternating hydrogen and fluorine bridges that arise as hydride and fluoride are successively exchanged and the center of positive charge alternates between carbon and silicon. Various product ions may be formed by random unimolecular break-up of the complex at various stages. Those ionic products actually observed are underlined.

In confirmation of the mechanism proposed in Figure 1 is the fact that the same extensive redistribution products are formed in SiH_3^+ collisions with CF_3H , a system which results in the same intermediate collision complex and presumably the same mechanism. The entrance into the mechanistic sequence from these reactants is shown in the upper right of Figure 1. It is interesting that the extensive redistribution products are definitely not observed in collisions of SiH_3^+ with CF_4 .

The fall-off in yield of CH_3^+ and CH_2F^+ at the higher energies (Table I) is in accord with a shorter complex lifetime and the existence of more energetically feasible reaction channels, as the internal energy of the complex is increased.

Table I

 ^{28}Si -monoisotopic Mass Spectra of $\text{CF}_3^+ + \text{SiH}_4$ Reaction

$\left(\frac{m}{e}\right)$	Ion	Relative Intensity at Barycentric Energy		
		1.3 eV	3.2 eV	9.5 eV
12	C^+	-	-	3
13	CH^+	-	0.5	14
14	CH_2^+	-	0.5	3
15	CH_3^+	18	17	3
29	SiH^+	11	24	215
30	SiH_2^+	15	49	150
31	SiH_3^+	1000	1000	1000
33	CFH_2^+	17	a	a
47	SiF^+	6	12	135
49	SiH_2F^+	69	262	438
50	CF_2^+	40	54	244
51	CF_2H^+	283	307	250
67	SiHF_2^+	b	b	b

a. Definitely present but obscured by isotopic contribution of $^{30}\text{SiH}_3^+$.

b. Definitely present but not measurable quantitatively due to proximity of CF_3^+ reactant ion.

Figure 1

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4.. ION-MOLECULE REACTIONS IN SiH_4 - CF_4 MIXTURES.

The reactions of ions derived from SiH_4 with CF_4 and of ions derived from CF_4 with SiH_4 have been identified and the reaction cross-sections determined over the range of 1-4 eV in the laboratory system. The results, in terms of reaction cross-sections at 1 eV are shown in Tables I and II. Phenomenological rate constants are compared with Langevin theory¹ in Table III.

It is clear from the data in these tables that the major reaction of positive ions containing fluorine with SiH_4 is H^- abstraction²⁻⁴ to yield SiH_3^+ , and the major reaction of positive silicon ions with CF_4 is F^- abstraction to yield CF_3^+ . In the collision of CF_3^+ and CF_2^+ with SiH_4 products are observed in which extensive redistribution of F and H between carbon and silicon centers has occurred. As described, in Topic 3 for the case of CF_3^+ ions, this redistribution must occur within a single collision complex.

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TABLE I

Reactions of Silicon-Containing Ions^a with CF₄^b

Reactant Ion (m/e)	Major Reactant Ion	Cross-Section in Å ² for Formation of Product Ion having m/e:					
		<u>47</u>	<u>48</u>	<u>49</u>	<u>50</u>	<u>51</u>	<u>69</u>
28	²⁸ Si ⁺ (100%)	3.9					0.36
29	²⁸ SiH ⁺ (96%)	0.43	0.06				0.53
30	²⁸ SiH ₂ ⁺ (98%)	0.14	0.09	1.1	0.17	0.03	4.4
31	²⁸ SiH ₃ ⁺ (94%)			0.68		0.40	7.2

^a Reactant-Ion Energy of 1.0 eV (Laboratory)^b Collision-chamber pressure of 1.0 x 10⁻³ torr

Table II

Reactions of Fluorine-Containing Ions^a with SiH₄^b

Reactant Ion	Target Molecule	Cross-Section in Å ² for Formation of Product Ion having m/e:											
		15	28	29	30	31	33	32	34	47	49	51	80
F ⁺	SiH ₄		0.5	1.0	0.5	0.9				0.7			
CF ⁺	SiD ₄							2	15	1.3		0.18	
CF ₂ ⁺	SiH ₄	0.38				33				13 ^c		10 ^c	0.08
CF ₃ ⁺	SiH ₄	0.67				37	1.0			0.1	1.7	10	

^aReactant-Ion Energy of 1.0 eV (Laboratory) unless otherwise indicated.

^bCollision-Chamber pressure of 1.0×10^{-3} torr unless otherwise indicated.

^cEstimated from data at 4 eV (Laboratory) for CF₃⁺ + SiD₄ system.

Table III

Total Reaction Cross-Sections and PhenomenologicalRate Constants^a

<u>Reactants</u>	<u>σ_{Total} in $\text{\AA}^2$</u>	<u>$k \times 10^{10}$ cm^3/sec</u>	<u>$k_{\text{Langevin}} \times 10^{10}$ cm^3/sec</u>
$\text{Si}^+ + \text{CF}_4$	4.3	1.1	8.6
$\text{SiH}^+ + \text{CF}_4$	1.0	0.3	8.5
$\text{SiH}_2^+ + \text{CF}_4$	5.9	1.5	8.4
$\text{SiH}_3^+ + \text{CF}_4$	8.7	2.2	8.3
$\text{F}^+ + \text{SiH}_4$	3.6	1.1	15.8
$\text{CF}^+ + \text{SiD}_4$	19	4.7	13.4
$\text{CF}_2^+ + \text{SiH}_4$	57	11	12.4
$\text{CF}_3^+ + \text{SiH}_4$	39	6.5	11.7

^aAt 1 eV reactant ion energy (Lab.)

5. DIRECT DETECTION OF ENERGY-RICH COMPLEXES IN THE REACTIONS OF Si^+ , SiH^+ and SiH_3^+ WITH BENZENE.

Although the direct detection of energy-rich collision complexes has been reported in studies of the pressure dependence of mass spectra,¹⁻⁴ instances of such detection in beam studies of ion-molecule reactions or of neutral-neutral reactions are rare. To our knowledge only two examples have appeared in the literature: (1) a collision complex with lifetime of at least 10^{-5} seconds was observed⁵ in the reaction of SiH_3^+ ions with C_2H_4 ; (2) collision complexes having lifetimes greater than 10^{-4} seconds have been detected⁶ in collisions of Rb atoms with $(\text{CH}_3\text{I})_n$ for $n \geq 3$. We wish to report here the direct detection of three energy-rich collision complexes that are formed in the collisions of beams of Si^+ , SiH^+ , and SiH_3^+ with C_6H_6 .

Ions formed from SiH_4 in an electron-impact ion source were mass-selected by a quadrupole mass filter and injected at center-of-mass energies of 0.7-7 eV into a collision chamber containing C_6H_6 . The ions produced in the collisions were mass-analyzed by a second mass filter and detected by an electron multiplier.

When Si^+ , SiH^+ and SiH_3^+ ions, having kinetic energies of 4 eV (Laboratory) or less, are injected into C_6H_6 at 1.0×10^{-3} torr, the respective collision complexes SiC_6H_6^+ (m/e 106), SiC_6H_7^+ (m/e 107), and SiC_6H_9^+ (m/e 109) are observed unambiguously at the detector after an ion-flight time of $\sim 2 \times 10^{-5}$ seconds. The major ionic products observed, in addition to the collision complexes, are in all cases C_6H_6^+ ions and those ions corresponding to loss of H from SiC_6H_6^+ , loss of H and H_2 from SiC_6H_7^+ , and loss of H_2 from

SiC_6H_9^+ . No collision complex is observed under these conditions in collisions of SiH_2^+ with C_6H_6 .

The effect of pressure on the reaction of SiH_3^+ ions, at 1 eV (Lab), with C_6H_6 is shown in Figure 1(a), in which the % of ionic products (uncorrected for isotopic contributions) is plotted versus the pressure of C_6H_6 . It is clear from this figure that the SiC_6H_9^+ (m/e 109) collision complexes can be stabilized against dissociation to C_6H_6^+ (m/e 78) + SiH_3 and to SiC_6H_7^+ (m/e 107) + H_2 . It is also clear from this figure that in the limit of zero pressure, i.e. no third-body stabilization, appreciable numbers of energy-rich collision complexes (energized molecules in the terminology of unimolecular reaction rate theory⁷) are reaching the detector and therefore have lifetimes in excess of 2×10^{-5} seconds. In Figure 1(b) is shown the effect of the relative kinetic energy of reactants for a C_6H_6 pressure of 1.0×10^{-3} torr. As expected, the relative abundance of the complex (m/e 109) decreases rapidly with increasing collision energy and the major channel opening up is that of the endoergic charge transfer to form C_6H_6^+ (m/e 78). The effects of pressure and collision energy on complex detection in the reactions of Si^+ and SiH^+ with C_6H_6 are completely analogous and it is noteworthy that the charge transfer from these ions to C_6H_6 is also endoergic. In the case of reaction of SiH_2^+ , the exoergic charge transfer is very fast and only small amounts of pressure-stabilized collision complexes are observed at pressure above 6×10^{-3} torr.

Application of the pertinent isotope corrections to Figure 1(a) - (i.e. $^{29}\text{SiH}_2^+$ makes up 6.4% of the m/e 31 beam and at 1 eV some 40% of the m/e 78 formed is due to charge transfer from this ion) - and extrapolation to zero pressure permits estimation to be made of the

fraction of energy-rich collision complexes that exist 2×10^{-5} seconds after formation. Neglecting reaction back to reactants, it is easy to show that this fraction F is related to the average complex lifetime τ by the expression

$$F = e^{-t/\tau} \quad (1)$$

where t is the ionic flight time of 2×10^{-5} seconds. The fractions of the three complexes remaining and the mean lifetimes at 0.7 eV center-of-mass energy are shown in Table I.

TABLE I *

Average Lifetimes of Energy-Rich Complexes at 0.7 eV Collision Energy

Reactants	Complex	F	τ (microseconds)
$\text{Si}^+ + \text{C}_6\text{H}_6$	SiC_6H_6^+	0.35	19
$\text{SiH}^+ + \text{C}_6\text{H}_6$	SiC_6H_7^+	0.13	9.8
$\text{SiH}_3^+ + \text{C}_6\text{H}_6$	SiC_6H_9^+	0.17	11

When SiD_3^+ ions at 1 eV (Lab) are injected into C_6H_6 it is found that 77% of the benzene ions are C_6H_6^+ , and 23% are $\text{C}_6\text{H}_5\text{D}^+$, while no significant amounts of $\text{C}_6\text{H}_4\text{D}_2^+$ are detected. The hydrogen-loss process undergone by the complex produces at least 70% HD. These facts indicate that in the complex the SiD_3^+ retains its identity, with very little exchange with the ring hydrogens occurring, and that a 1,2 molecular hydrogen elimination occurs to form HD and the $\text{C}_6\text{H}_5\text{SiD}_2^+$ ion. It is thus strongly suggested that the collision complex is a dienyl cation⁸ analogous to the intermediates proposed in classical liquid-phase studies of the addition of carbonium ions to aromatics, and that the reaction proceeds as shown in (2) and (3).

The benzyl-type structure of the product of (3) has been previously proposed in mass-spectrometric studies of phenylsilane.⁹

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Figure 1

6. ION-MOLECULE REACTIONS IN $\text{SiH}_4\text{-C}_6\text{H}_6$ MIXTURES

The reactions of ions derived from SiH_4 with C_6H_6 and of ions derived from C_6H_6 with SiH_4 have been identified and the respective reaction cross-sections have been measured as functions of ion kinetic energy and neutral molecule density. The major reactions, expressed in terms of cross-sections of product ions of given m/e, are shown in Tables I and II. Phenomenological rate constants determined at 1 eV ion-energy in the laboratory system are given in Table III.

As discussed in Topic 5, Si^+ , SiH^+ and SiH_3^+ form energy-rich collision complexes with C_6H_6 that are sufficiently long-lived for them to survive the transit time of $\sim 10^{-5}$ seconds to the detector of the apparatus. SiH_2^+ does not form a complex of sufficient lifetime to reach the detector, but undergoes principally exothermic charge transfer to yield C_6H_6^+ and SiH_2 . Ions derived from C_6H_6 do not react extensively with SiH_4 but the major reaction of all such ions is to abstract a hydride ion to form SiH_3^+ .

TABLE I
Reactions of Silicon-Containing Ions^a with C₆H₆^b

Reactant Ion	Cross-Section in Å ² for Formation of Product Ion of m/e								
	<u>78</u>	<u>79</u>	<u>81</u>	<u>83</u>	<u>105</u>	<u>106</u>	<u>107</u>	<u>108</u>	<u>109</u>
Si ⁺	4.6				3.8	7.4			
SiH ⁺	14	2.2	3.6		6.6	1.4	6.7		
SiH ₂ ⁺	75	6.0			2.6	33	18		
SiH ₃ ⁺	8.0	1.5	2.8	1.0			8.6		18

^aReactant-Ion Energy of 1.0 eV in the laboratory frame of reference.

^bCollision chamber pressure of 1.0x10⁻³ torr.

TABLE II

Reactions of Ions derived from $C_6H_6^a$ with SiH_4^b

Reactant Ion	Cross-Section in $\text{\AA}^2$ for Formation of Product Ion of m/e											
	31	33	39	42	43	52	53	54	55	56	57	67
$C_4H_2^+$	8.9	-	-	1.6	2.0	-	2.8	3.9	6.5	2.2	0.2	3.4
$C_4H_3^+$	5.6	0.6	-	-	1.1	-	-	0.1	2.3	-	2.1	0.2
$C_4H_4^+$	1.4	-	-	0.6	1.2	-	-	-	1.2	2.3	0.5	0.5
$C_6H_5^+$	9.6	-	-	-	0.3	-	-	-	-	-	-	-
$C_6H_6^+$	3.8	-	0.2	-	-	0.5	-	-	-	-	-	-

^aReactant-Ion Energy of 1.0 eV in the laboratory frame of reference.^bCollision chamber pressure of 1.0×10^{-3} torr.

Table III

Phenomenological Rate Constants^a in $\text{SiH}_4\text{-C}_6\text{H}_6$ System for 1 eV-Ions

Reaction	$k \times 10^{10} (\text{cm}^3/\text{sec})$	$k \times 10^{10} (\text{Langevin}) \text{cm}^3/\text{sec}$
$\text{Si}^+ + \text{C}_6\text{H}_6 \rightarrow \text{Products}$	4.2	16.6
$\text{SiH}^+ + \text{C}_6\text{H}_6 \rightarrow \text{Products}$	8.9	16.4
$\text{SiH}_2^+ + \text{C}_6\text{H}_6 \rightarrow \text{Products}$	34	16.2
$\text{SiH}_3^+ + \text{C}_6\text{H}_6 \rightarrow \text{Products}$	10	16.0
$\text{C}_6\text{H}_5^+ + \text{SiH}_4 \rightarrow \text{Products}$	1.6	11.5
$\text{C}_6\text{H}_6^+ + \text{SiH}_4 \rightarrow \text{Products}$	0.7	11.5
$\text{C}_4\text{H}_2^+ + \text{SiH}_4 \rightarrow \text{Products}$	6.2	12.4
$\text{C}_4\text{H}_3^+ + \text{SiH}_4 \rightarrow \text{Products}$	2.3	12.3
$\text{C}_4\text{H}_4^+ + \text{SiH}_4 \rightarrow \text{Products}$	1.5	12.3

^aUncertainty in k is assumed to be $\pm 30\%$, the same as in the cross-section

7. REACTION RATE CONSTANTS FOR H-ATOM INDUCED DECOMPOSITION

Very little information exists in the literature with respect to the reaction rates of hydrogen atoms with silanes and germanes and moreover most information that is available refers to D-atoms rather than H-atoms. During the studies of the H-atom initiated decomposition of SiH_4 (described as Topic 1 in this report) it occurred to us that we could determine rate constants of such reactions at ambient temperature, relative to a standard reaction, mass spectrometrically.

Consider a system composed of 98% H_2 with the remainder being comprised of a Group IV hydride, $\equiv\text{M}-\text{H}$ ($\text{M}=\text{Si}, \text{Ge}$), C_2H_4 , and mercury vapor. Irradiation with 2537 Å radiation results in the following reactions:

The rates of reactions (3) and (4) can be determined by straightforward measurements, as a function of time, of the relative concentrations of $\equiv\text{M}-\text{H}$ and C_2H_4 only if the free-radicals $\equiv\text{M}\cdot$ and C_2H_5 can be intercepted and prevented from reacting with $\equiv\text{M}-\text{H}$, C_2H_4 and each other. On the basis of our previous studies^{1,2} NO at a level of ~0.5% would appear to be an excellent interceptor. With NO present we must add (5) and (6) to the above scheme. The products of (5) and (6) will react further but provided we measure initial rates of loss

of $\equiv M-H$ and C_2H_4 , the ratio $\frac{k_3}{k_4}$ may be obtained without interference from secondary processes.

From the mechanism (1)-(6) we have

$$-\frac{d[\equiv M-H]}{dt} = k_3 [H] [\equiv M-H] \quad (7)$$

$$-\frac{d[C_2H_4]}{dt} = k_4 [H] [C_2H_4] \quad (8)$$

Introducing the initial concentrations $[\equiv M-H]_0$ and $[C_2H_4]_0$ and the mass-spectrometric relationship between concentration and intensity of an ion, we have (9) and (10). These simple

$$\frac{[\equiv M-H]}{[\equiv M-H]_0} = \frac{i_m}{i_m^0} \quad (9)$$

$$\frac{[C_2H_4]}{[C_2H_4]_0} = \frac{i_s}{i_s^0} \quad (10)$$

expressions are valid provided m is a mass unique to $\equiv M-H$ and S is a mass unique to C_2H_4 . Substitution of (9) and (10) into (7) and (8) yields

$$\left(\frac{1}{i_m^0} \right) \left(\frac{di_m}{dt} \right) = k_3 [H] \frac{[\equiv M-H]}{[\equiv M-H]_0} \quad (11)$$

$$\left(\frac{1}{i_s^0} \right) \left(\frac{di_s}{dt} \right) = k_4 [H] \frac{[C_2H_4]}{[C_2H_4]_0} \quad (12)$$

and upon passing to limit of $t \rightarrow 0$ we obtain

$$\frac{1}{i_m^0} \left(\frac{di_m}{dt} \right)_{t \rightarrow 0} = k_3 [H] \quad (13)$$

$$\left(\frac{1}{i_m^0} \right) \left(\frac{di_s}{dt} \right)_{t \rightarrow 0} = k_4 [H] \quad (14)$$

Thus by measuring the initial slopes of plots of i_m and i_s versus t , we obtain by division of (13) by (14)

$$\left(\frac{i_s^0}{i_m^0} \right) \left(\frac{\left(\frac{di_m}{dt} \right)_0}{\left(\frac{di_s}{dt} \right)_0} \right) = \frac{k_3}{k_4} \quad (15)$$

the ratio k_3/k_4 . Since k_4 is known we thus may obtain an absolute value for k_3 .

Results of such experiments at 30°C. are given in Table I.

The rate constants for H-atom attack on SiH_4 and SiD_4 are in satisfactory agreement with the results of Potzinger et al.^{8,12} but much lower than the values reported by Cowfer, Lynch and Michael⁹ and Choo, Gaspar and Wolf.¹⁰ The rate constants for H-atom attack on Si_2H_6 and Si_2D_6 are in satisfactory agreement with the value reported by Pollock, Sandhu, Jodhan and Strausz.¹¹ The method therefore appears to be a very useful one to study reactions involving H-atom attack.

TABLE I.

Reaction Rate Constants at Room Temperature

<u>Series</u>	<u>Decomposition Reaction</u>	<u>Relative k</u>	<u>$k \times 10^{13} (\text{cm}^3/\text{sec})$ This Work</u>	<u>$k \times 10^{13} (\text{cm}^3/\text{sec})$ Literature</u>
A	$\text{H} + \text{C}_2\text{H}_4$	1		$12.1 \pm 2.2^{3-7}$
	$\text{H} + \text{SiH}_4$	0.524 ± 0.084	6.3 ± 1.5	$4.5 \pm 0.2^8, 26^9, 85 \pm 7^{10}$
	$\text{H} + \text{CH}_3\text{SiH}_3$	0.73^a	8.8	
	$\text{H} + (\text{CH}_3)_2\text{SiH}_2$	0.72 ± 0.16	8.7 ± 2.5	
	$\text{H} + (\text{CH}_3)_3\text{SiH}$	0.673 ± 0.057	8.1 ± 1.6	
	$\text{H} + \text{Si}_2\text{H}_6$	4.39 ± 0.62	53 ± 12	36^{11}
	$\text{H} + \text{SiD}_4$	0.176 ± 0.010	2.13 ± 0.41	$2.71 \pm 0.53^{12}, 1.8^8$
	$\text{H} + \text{CH}_3\text{SiD}_3$	0.273 ± 0.024	3.30 ± 0.67	
	$\text{H} + \text{Si}_2\text{D}_6$	1.85 ± 0.05	22.4 ± 4.1	23^{11}
B	$\text{H} + (\text{CH}_3)_3\text{SiH}$	1	8.1 ± 1.6	
	$\text{H} + \text{SiH}_4$	0.742 ± 0.089	6.0 ± 1.4	$4.5 \pm 0.2^8, 26^9, 85 \pm 7^{10}$
	$\text{H} + (\text{CH}_3)_2\text{SiH}_2$	1.16 ± 0.04	9.4 ± 1.9	

TABLE I (Continued)

<u>Series</u>	<u>Decomposition Reaction</u>	<u>Relative k</u>	<u>$k \times 10^{13} (\text{cm}^3/\text{sec})$ This Work</u>	<u>$k \times 10^{13} (\text{cm}^3/\text{sec})$ Literature</u>
C	$\text{H} + \text{Si}_2\text{H}_6$	1	53 ± 12	36"
	$\text{H} + \text{GeH}_4$	0.370 ± 0.025	20 ± 4	
	$\text{H} + \text{Ge}_2\text{H}_6$	1.36 ± 0.09	72 ± 16	

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8. γ -RAY RADIOLYSIS OF SiH_4 -NO MIXTURES

In the γ -ray radiolysis of monosilane, disilane is formed by a free-radical path involving reactions (1) and (2),

which were discussed in Topic 1 of this report. If this were the sole mode of formation of disilane, the addition of free-radical scavengers would reduce $G(\text{Si}_2\text{H}_6)$ to zero. The use of NO as a radical scavenger yields the data depicted in Table 1 which show that $G(\text{Si}_2\text{H}_6)$ can be reduced only to 2.3 ± 0.1 from the value of 5.3 ± 0.5 that obtains in the absence of free-radical scavenger. The 43% residual yield in the radiolysis is in excellent agreement with the SiH_3 -radical scavenging experiments using ethylene that were reported some years ago.¹ The residual yield of disilane in the radiolysis, which does not exist in the Hg-photosensitized decomposition of monosilane,² is undoubtedly due to the ionic sequence³ (3)-(5)

Our major interest in this system is to study the radiolytically induced reactions of SiH_3^+ with such substrates as C_2H_4 , CF_4 , and C_6H_6 and in order to accomplish this it is necessary to insure complete interception of SiH_3 and other free radicals such as C_2H_5

and CF_3 . The data of Table I and the results of previous studies^{4,5} indicate that ~10% of NO will accomplish this interception.

Studies during the report period of the effect of NO concentration have confirmed our earlier report⁶ of the nature and yields of the products of the SiH_4 -NO radiolysis. The radiolytic decomposition of SiH_4 in the presence of NO is a free-radical chain reaction² in which the major products are N_2O , $\text{SiH}_3\text{OSiH}_3$, $\text{SiH}_3\text{OSiH}_2\text{OSiH}_3$ and $\text{SiH}_3\text{OSiH}_2\text{OSiH}_2\text{OSiH}_3$. G-values for 100 torr of SiH_4 and several NO partial pressures are shown in Table II.

TABLE I

Dependence of $G(\text{Si}_2\text{H}_6)$ on NO Partial Pressure: ($P_{\text{SiH}_4} = 100$ torr)

<u>(NO) (torr)</u>	<u>$G(\text{Si}_2\text{H}_6)$</u>
0	5.3
2	4.5
5	4.7
10	2.2
20	2.4

TABLE II

G-Value in SiH₄-NO Radiolysis

<u>Molecule</u>	<u>G(molecule/100 eV)</u>		
	<u>P(NO)=0</u>	<u>P(NO)=5 torr</u>	<u>P(NO)=20 torr</u>
H ₂	14.8	15.5	12.7
NO	-	-48	-54
SiH ₄	-34	-53	-82
N ₂ O	-	21	16
Si ₂ H ₆	5.3	4.7	2.4
(SiH ₃) ₂ O	-	7.6	4.4
(SiH ₃ O) ₂ SiH ₂	-	1.8	1.5
(SiH ₃) ₃ SiH	-	0.5	0.3

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ANNUAL LIST OF REPRINTS, PREPRINTS, THESES, LECTURES, ETC.

A. Reprints.

E. R. Austin and F. W. Lampe, "Mercury-Photosensitized Reaction of Silyl Radicals", J. Photochem. 5, 155 (1976).

B. Preprints

1. E. R. Austin and F. W. Lampe, "Hydrogen-Atom Initiated Decomposition of Monosilane", J. Phys. Chem., IN PRESS.
2. W. N. Allen and F. W. Lampe, "Direct Detection of Energy-Rich Collision Complexes in the Reactions of Si^+ , SiH^+ and SiH_3^+ with Benzene, J. Chem. Phys., IN PRESS.
3. W. N. Allen, T. M. H. Cheng, F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-D}_2$ Mixtures", J. Chem. Phys. IN PRESS.
4. J. R. Krause and F. W. Lampe, "Extensive Redistributions of Fluorine and Hydrogen in the Reaction of CF_3^+ with SiH_4 ". J. Am. Chem. Soc., SUBMITTED.
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C. Lectures

1. F. W. Lampe, "Mercury Photosensitized Reactions of Silyl Radicals", VIII International Conference on Photochemistry, The University of Alberta, Edmonton, Alberta, Canada. August 8, 1975.
2. E. R. Austin, "Hydrogen-Atom Initiated Decomposition of Monosilane", 12th Informal Conference on Photochemistry, Gaithersburg, Maryland, June 29, 1976.
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4. F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-CF}_4$ Mixtures". American Chemical Society Meeting, San Francisco, California, September 1, 1976.

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