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SILANES AND GERMANES

Progress Report

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Preface

Our continuing study of the radiation-induced decompositions of silane and germane systems may be subdivided into three types of investigation as follows:

A. Photochemical Decompositions

Initiation of the decomposition of silanes and germanes by direct photolysis and by photosensitization techniques is carried out in flow systems that are analyzed continuously by mass spectrometry. In these investigations, the mechanisms of the purely free-radical decomposition paths can be identified and their details elucidated. The knowledge obtained in these studies is essential to an understanding of the photochemistry, radiation chemistry and electric discharge chemistry of the volatile silanes and germanes.

B. Ion-Molecule Reactions

Identification and study of the ion-molecule reactions characteristic of silane and germane systems are conducted using the techniques of tandem and high-pressure mass spectrometry. The fundamental information so acquired is of considerable importance to our growing knowledge of thermochemistry, kinetics, and dynamics of reactive collisions. It is also essential in providing a basis for the interpretation and understanding of chemical decompositions that are induced by ionizing radiation.

C. Gamma and Ultraviolet Irradiations of Static Systems

Radiolyses and photolyses of silanes and germanes and of mixtures of these substances with noble gases, organic compounds, free-radical scavengers, and ion scavengers are carried out in static systems using a Co^{60} -source and various ultraviolet light sources, respectively. The irradiations are

followed by product analyses, using mass spectrometric and gas chromatographic techniques, to determine radiation yields and quantum yields as functions of experimental conditions. Mechanistic conclusions are drawn from the dependence of the radiation and quantum yields on reaction conditions, utilizing knowledge of pertinent elementary processes drawn from A and B above.

In a program such as this 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 September 1, 1978 to August 31, 1979. During the report year the emphasis was almost equally divided between phases A and B. This report consists of abstracts of the studies carried out in the various topics during the report-year.

1. REACTIONS OF METHYL CATIONS WITH ETHYLSILANES

EY-76-S-02-3416-10, J. Am. Chem. Soc., 101, xxxx (1979)

The gas-phase reactions of CH_3^+ with $(\text{C}_2\text{H}_5)_n\text{SiH}_{4-n}$ ($n=1,2,3,4$) have been studied in a tandem mass-spectrometric apparatus. Exothermic reactions and cross-sections observed for reactant ion energies of 1 eV in the laboratory frame of reference are shown in Table 1. Endothermic reactions observed and the cross-sections at 1 eV are shown in Table 2. All cross-sections have been corrected for the naturally occurring ^{29}Si , ^{30}Si and ^{13}C isotopes.

The major reactions as seen in Table 1 are charge transfer, hydride ion transfer and ethide ion (C_2H_5^-) transfer from the target silane molecule to the attacking CH_3^+ ion. A rather surprising result is that, except for the case of $\text{C}_2\text{H}_5\text{SiH}_3$, ethide ion transfer is the predominant process.

Isotopic labelling of the reactant ions show only very minor incorporation of the label into the ionic products. For example, the effect of replacement of $^{12}\text{CH}_3^+$ by $^{13}\text{CH}_3^+$ and $^{12}\text{CD}_3^+$ on the mass spectrum of the major products in the reaction of methyl cations with triethyl silane is to be seen in Figure 1. The essential identity of the three spectra indicates that the major reactions are the abstraction of negative ions from the silanes. Further the results suggest that the predominant part of these major reactions of hydride ion abstraction, ($M/e=115$ amu) ethide ion abstraction ($M/e=87$ amu), and the more complicated process to yield $M/e=59$ amu are either direct processes or proceed through collision complexes that do not involve pentavalent silicon.

TABLE 1

Major Reactions of CH_3^+ with Ethyl Silanes at 1 eV (Laboratory)

Reaction No.	Reaction	ΔH° (kcal)	$\sigma(\text{\AA}^2)$	$10^9 k(\text{cm}^3/\text{sec})$
3	$\text{CH}_3^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{C}_2\text{H}_5\text{SiH}_3^+ + \text{CH}_3$	--	4.9	0.18
4	$\text{CH}_3^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{C}_2\text{H}_5\text{SiH}_2^+ + \text{CH}_4$	--	80	2.8
5	$\text{CH}_3^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{C}_2\text{H}_6$	-57 ^a	11	0.39
6	$\text{CH}_3^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{SiH}_3^+ + \text{C}_3\text{H}_8$	-38 ^a	22	0.79
7	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_2\text{SiH}_2 \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}_2^+ + \text{CH}_3$	+1	42	1.5
8	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_2\text{SiH}_2 \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}^+ + \text{CH}_4$	--	22	0.79
9	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_2\text{SiH}_2 \rightarrow \text{C}_2\text{H}_5\text{SiH}_2^+ + \text{C}_3\text{H}_8$	--	87	3.1
10	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow (\text{C}_2\text{H}_5)_3\text{SiH}^+ + \text{CH}_3$	-8	35	1.3
11	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow (\text{C}_2\text{H}_5)_3\text{Si}^+ + \text{CH}_4$	-90	3.9	0.14
12	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}^+ + \text{C}_3\text{H}_8$	--	74	2.7
13	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow (\text{C}_2\text{H}_5)_2\text{Si}^+ + \text{CH}_4 + \text{C}_2\text{H}_5$	-7	14	0.50
14	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow \text{C}_2\text{H}_5\text{SiH}_2^+ + \text{CH}_4 + 2\text{C}_2\text{H}_4$	--	17	0.61
15	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow (\text{C}_2\text{H}_5)_4\text{Si}^+ + \text{CH}_3$	-22	10	0.36
16	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow (\text{C}_2\text{H}_5)_3\text{Si}^+ + \text{C}_3\text{H}_8$	-80	91	3.3
17	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}^+ + \text{C}_3\text{H}_8 + \text{C}_2\text{H}_4$	--	11	0.39

^aEstimated using the bond energy scheme of Allen⁷ with the data of Potzinger, Ritter and Krause³ to calculate $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{SiH}_3)$.

TABLE 2

Endothermic Reactions of CH_3^+ with Ethyl Silanes at 1 eV (Laboratory)

<u>Reaction No.</u>	<u>Reaction</u>	<u>ΔH° (kcal)</u>	<u>$\sigma(\text{\AA}^2)$</u>
20	$\text{CH}_3^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{C}_2\text{H}_5\text{SiH}^+ + \text{CH}_3 + \text{H}_2$	--	0.6
21	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow \text{C}_2\text{H}_5\text{SiH}^+ + \text{C}_4\text{H}_{10} + \text{C}_2\text{H}_4$	--	5.7
22	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{CH}_3 + \text{C-C}_6\text{H}_{12}$	+16	1.2
23	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow \text{SiH}_3^+ + \text{C-C}_6\text{H}_{12} + \text{C}_2\text{H}_5$	+32	0.4
24	$\text{CH}_3^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow \text{C}_2\text{H}_3^+ + (\text{C}_2\text{H}_5)_3\text{SiCH}_3 + \text{H}_2$	+25	0.4

Figure 1.

2. REACTIONS OF ETHYL, PROPYL AND BUTYL CATIONS WITH METHYL AND ETHYLSILANES

EY-76-02-3416-11, J. Am. Chem. Soc., 101, xxxx (1979).

The gas-phase reactions of C_2H_5^+ , $\text{sec-C}_3\text{H}_7^+$ and $\text{t-C}_4\text{H}_9^+$ with $(\text{CH}_3)_n\text{SiH}_{4-n}$ and of C_2H_5^+ with $(\text{C}_2\text{H}_5)_n\text{SiH}_{4-n}$ ($n=0,1,2,3,4$) have been studied in a tandem mass-spectrometric apparatus.

Reaction cross-sections at 1 eV kinetic energy in the laboratory frame of reference have been determined for the exothermic reactions of C_2H_5^+ with the various silanes. These data are shown in Tables 3 and 4.

The predominant processes are hydride ion and alkide ion (CH_3^- or C_2H_5^-) transfer from the silane to the attacking ion with the alkide ion transfer becoming the most probable process when the number of alkyl groups in the silane is three or four. The reaction energetics prove that CH_3^- and C_2H_5^- transfer occurs as a simple exchange of the molecular anion between reactants. That is, in the case of the reaction of C_2H_5^+ with $(\text{CH}_3)_2\text{SiH}_2$, the known standard enthalpies of formation of the possible products and the experimental observation that formation of $\text{CH}_3\text{SiH}_2^+$ is exothermic require the reaction to be

which is a simple exchange of the CH_3^- moiety between reactants.

Product ion distributions have been determined for the reactions of $\text{sec-C}_3\text{H}_7^+$ and $\text{t-C}_4\text{H}_9^+$ ions, having 1 eV of kinetic energy in the laboratory system, with the silane series $(\text{CH}_3)_n\text{SiH}_{4-n}$, $n=1,2,3,4$.

TABLE 3

MAJOR REACTIONS OF ETHYL CATIONS WITH MONOSILANE AND METHYL SILANES AT 1 eV (LAB)

Reaction No.	Reaction	ΔH° (kcal.)	$\sigma(\text{\AA}^2)$	$10^9 k(\frac{\text{cm}^3}{\text{sec}})$
3	$\text{C}_2\text{H}_5^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{C}_2\text{H}_6$	-8	51	1.3
4	$\text{C}_2\text{H}_5^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{C}_2\text{H}_6$	-20	81	2.1
5	$\text{C}_2\text{H}_5^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{SiH}_3^+ + \text{C}_3\text{H}_8$	-1	9.3	0.24
6	$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_2\text{SiH}_2 \rightarrow (\text{CH}_3)_2\text{SiH}^+ + \text{C}_2\text{H}_6$	-35	62	1.6
7	$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_2\text{SiH}_2 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{C}_3\text{H}_8$	-12	50	1.3
9	$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_3\text{SiH} \rightarrow (\text{CH}_3)_3\text{Si}^+ + \text{C}_2\text{H}_6$	-49	22	0.57
10	$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_3\text{SiH} \rightarrow (\text{CH}_3)_2\text{SiH}^+ + \text{C}_3\text{H}_8$	-27	91	2.3
13	$\text{C}_2\text{H}_5^+ + (\text{CH}_3)_4\text{Si} \rightarrow (\text{CH}_3)_3\text{Si}^+ + \text{C}_2\text{H}_6$	-46	99	2.6

TABLE 4

MAJOR REACTIONS OF ETHYL CATIONS WITH ETHYL SILANES AT 1 eV (LAB)

Reaction No.	Reaction	ΔH° (kcal.)	$\sigma(\text{\AA}^2)$	$10^9 k(\frac{\text{cm}^3}{\text{sec}})$
14	$\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{C}_2\text{H}_5\text{SiH}_2^+ + \text{C}_2\text{H}_6$	-16 ^{a,b}	102	
15	$\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_5\text{SiH}_3 \rightarrow \text{SiH}_3^+ + \text{C}_4\text{H}_{10}$	-2 ^a	6.5	
16	$\text{C}_2\text{H}_5^+ + (\text{C}_2\text{H}_5)_2\text{SiH}_2 \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}^+ + \text{C}_2\text{H}_6$	-44 ^b	47	
17	$\text{C}_2\text{H}_5^+ + (\text{C}_2\text{H}_5)_2\text{SiH}_2 \rightarrow \text{C}_2\text{H}_5\text{SiH}_2^+ + \text{C}_4\text{H}_{10}$	-18 ^b	59	
18	$\text{C}_2\text{H}_5^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow (\text{C}_2\text{H}_5)_3\text{Si}^+ + \text{C}_2\text{H}_6$	-52	16	
19	$\text{C}_2\text{H}_5^+ + (\text{C}_2\text{H}_5)_3\text{SiH} \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}^+ + \text{C}_4\text{H}_{10}$	-38 ^b	62	
20	$\text{C}_2\text{H}_5^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow (\text{C}_2\text{H}_5)_3\text{Si}^+ + \text{C}_4\text{H}_{10}$	-45	58	
21	$\text{C}_2\text{H}_5^+ + (\text{C}_2\text{H}_5)_4\text{Si} \rightarrow (\text{C}_2\text{H}_5)_2\text{SiH}^+ + \text{C}_4\text{H}_{10} + \text{C}_2\text{H}_4$	-9 ^b	23	

(a) Estimated using the average CH_2 increment to ΔH_f° of neutral silane molecules of -3 kcal/mole^x.

(b) Estimated using the average CH_2 increment to ΔH_f° of ions derived from silanes of -8 kcal/mole^x.

The reactions identified are shown in Table 5. Absolute reaction cross-sections were not determined in these systems but the relative probabilities of occurrence are shown in Table 3 along with the standard enthalpy changes calculated from thermochemical data.

The total cross-sections for reaction of $\text{sec-C}_3\text{H}_7^+$ with the silanes are comparable to those for the reactions of C_2H_5^+ ; however, the total cross-sections for the reactions of $\text{t-C}_4\text{H}_9^+$ appear to be lower by 1-2 orders of magnitude.

The thermochemistry of hydride ion and methide ion transfer is summarized graphically in Figures 2 and 3.

TABLE 5

MAJOR REACTIONS OF PROPYL AND BUTYL IONS WITH METHYL SILANES AT 1 eV (LAB)

<u>Reaction No.</u>	<u>Reaction</u>	<u>ΔH^0(kcal.)</u>	<u>Relative Probability</u>
22	$(CH_3)_2CH^+ + CH_3SiH_3 \rightarrow CH_3SiH_2^+ + C_3H_8$	+2	38
23	$(CH_3)_2CH^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH^+ + C_3H_8$	-13	58
24	$(CH_3)_2CH^+ + (CH_3)_2SiH_2 \rightarrow CH_3SiH_2^+ + i-C_4H_{10}$	+9	3
25	$(CH_3)_2CH^+ + (CH_3)_3SiH \rightarrow (CH_3)_3Si^+ + C_3H_8$	-27	36
26	$(CH_3)_2CH^+ + (CH_3)_3SiH \rightarrow (CH_3)_2SiH^+ + i-C_4H_{10}$	-7	10
27	$(CH_3)_2CH^+ + (CH_3)_4Si \rightarrow (CH_3)_3Si^+ + i-C_4H_{10}$	-21	100
28	$(CH_3)_3C^+ + CH_3SiH_3 \rightarrow CH_3SiH_2^+ + i-C_4H_{10}$	+21	1
29	$(CH_3)_3C^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH^+ + i-C_4H_{10}$	+6	4
30	$(CH_3)_3C^+ + (CH_3)_3SiH \rightarrow (CH_3)_3Si^+ + i-C_4H_{10}$	-8	3
31	$(CH_3)_3C^+ + (CH_3)_3SiH \rightarrow (CH_3)_2SiH^+ + neo\ C_5H_{12}$	+9	0.3
32	$(CH_3)_3C^+ + (CH_3)_4Si \rightarrow (CH_3)_3Si^+ + neo\ C_5H_{12}$	-5	1

Thermochemistry of Hydride Transfer from $(\text{CH}_3)_n \text{SiH}_{4-n}$
to Alkyl Ions

Figure 2.

Figure 3.

3. THE 147-NANOMETER PHOTOLYSIS OF DISILANE

EY-76-S-02-3416-12, J. Am. Chem. Soc. (Submitted August 24, 1979)

The photodecomposition of Si_2H_6 at 147 nanometers results in the formation of H_2 , SiH_4 , Si_3H_8 , Si_4H_{10} , Si_5H_{12} and a solid film of amorphous silicon hydride (a-Si:H). Three primary processes are proposed to account for the results, namely, (a) $\text{Si}_2\text{H}_6 + h\nu \rightarrow \text{SiH}_2 + \text{H}$ ($\phi_a=0.61$); (b) $\text{Si}_2\text{H}_6 + h\nu \rightarrow \text{SiH}_3\text{SiH} + 2\text{H}$ ($\phi_b=0.18$); (c) $\text{Si}_2\text{H}_6 + h\nu \rightarrow \text{Si}_2\text{H}_5 + \text{H}$ ($\phi_c=0.21$). The overall quantum yields of the photodecomposition are shown in Table 6. From a material balance on the data at a partial pressure of Si_2H_6 of 1 torr the quantum yield for the deposition of silicon atoms on the vessel surfaces is $\phi(\text{Si}, \text{surface}) = 2.2$.

The mechanism proposed, which incorporates known reactions of the SiH_2 , SiH_3 , SiH_3SiH , and Si_2H_5 radicals, is shown to be in accord with the experimental facts and is presented below:

Table 6. Quantum Yields in the Photodecomposition of Si_2H_6 at 147 nm^a

Partial Pressure Si_2H_6 torr	$\phi(-\text{Si}_2\text{H}_6)$	$\phi(\text{SiH}_4)$	$\phi(\text{Si}_3\text{H}_8)$	$\phi(\text{Si}_4\text{H}_{10})^b$
0.50	4.1 $\pm$ 0.3		0.68 $\pm$ 0.08	0.59 $\pm$ 0.06
0.95	4.3 $\pm$ 0.2			
1.00		1.2 $\pm$ 0.4	0.91 $\pm$ 0.08	0.62 $\pm$ 0.03
1.95	4.1 $\pm$ 0.4		1.18 $\pm$ 0.19	0.63 $\pm$ 0.04
4.36	4.1 $\pm$ 0.2		1.20 $\pm$ 0.08	0.54 $\pm$ 0.03

(a) Diluent gas = He; total pressure of = 42 torr.

(b) This represents the total tetrasilane. We were unable to resolve the two isomers.

4. LIFETIMES AND COLLISIONAL STABILIZATION OF CHEMICALLY ACTIVATED ETHYLSILYL CATIONS

In earlier studies¹ of the reaction of SiH_3^+ with C_2H_4 we reported the direct detection and measurement of the lifetimes of the energy-rich $\text{C}_2\text{H}_5\text{SiH}_2^{+*}$, formed by chemical activation in the reaction

in the range of 1-3 eV of kinetic energy in the laboratory frame of reference. The interesting question of the dependence of the lifetime of $\text{C}_2\text{H}_5\text{SiH}_2^{+*}$, relative to its dissociation processes (2) and (3),

on the relative translational energy of the reactants was obscured by the very broad kinetic energy spread (~ 1 eV) of the reactant ions. This broad energy spread was characteristic of the original apparatus and it was to overcome this problem that the new tandem mass spectrometer described in last year's progress report (EY-76-S-02-3416-8) was constructed.

Studies of the reaction of SiH_3^+ with C_2H_4 in the new apparatus, in which the energy spread is 0.2 - 0.3 eV, have been initiated and are now in progress. A striking result is that at the lowest kinetic energies with the current apparatus, only minute amounts, if indeed any, of the unstabilized collision complexes $\text{C}_2\text{H}_5\text{SiH}_2^{+*}$

are detected. This is in contrast with the earlier results using the original apparatus, in which at the same nominal energies, significant amounts of unstabilized couples were detected. The most likely explanation is that it was just the large energy spread of the reactant ion beam in the original apparatus which permitted direct detection of the unstabilized collision complexes. Thus with a nominal reactant ion energy of 1 eV (Laboratory) in the original apparatus, a significant fraction of the ions in the beam had kinetic energies of just a few tenths of an electron volt, and it was the reaction of these low-energy SiH_3^+ ions with C_2H_4 that produced the directly detected collision complex. By contrast, with a nominal reactant ion-energy of 1 eV (Laboratory) in the present apparatus, only a negligible fraction of the ions in the beam have energies below 0.8 eV, and consequently the collision complex formed has a higher internal energy and a shorter lifetime with respect to dissociation.

While the direct detection of the unstabilized collision complex $\text{C}_2\text{H}_5\text{SiH}_2^{+*}$ is somewhat tenuous in the new apparatus, we are obtaining very interesting results on the collisional stabilization process. The data in Figure 4 show the fraction of ionic products that are of $m/e = 59$ ($\text{C}_2\text{H}_5\text{SiH}_2^+$), some 2×10^{-5} seconds after collision of SiH_3^+ with C_2H_4 , as a function of the pressure of C_2H_4 in the collision cell. At a low collision energy of 0.5 eV (center of mass) the stabilization curve (that is, $F(59)$ as a function of pressure) is concave downward from the low-pressure limit to the higher pressures at which a plateau near $F(59) = 0.8$ is approached. The initial linear rise of $F(59)$ with pressure indicates that with this much internal energy in $\text{C}_2\text{H}_5\text{SiH}_2^{+*}$ one collision is on the average sufficient

Figure 4.

for stabilization. At the much higher collision energy of 3.7 eV, F(50) increases, in the low pressure, region with a higher power of the pressure, indicating that, on the average, 2 or more collisions are necessary to stabilize the collision complex. Analysis of these curves, which is now in progress, will yield experimental values of the average energy transferred per collision as a function of internal energy of the complex. Moreover, additional studies are in progress using deactivation gases other than ethylene itself to determine how the structure of the stabilizing gas influences the energy transferred per collision.

References

1. W. N. Allen and F. W. Lampe, J. Am. Chem. Soc. 99, 6816 (1977).

5. FORMATION OF GeH_5^+ AND THE PROTON AFFINITY OF GeH_4

We have previously observed¹ GeH_4D^+ to be formed in a proton transfer reaction from D_3O^+ and D_3S^+ in the tandem mass spectrometer. The reactions, (1) and (2),

appear to be exothermic and therefore fix the lower limit of the proton affinity of GeH_4 at 170 kcal/mole. Attempts to determine whether ND_4^+ will proton transfer to GeH_4 have been inconclusive, although they have suggested that such a reaction is endothermic, the establishment of which would fix the upper limit of the proton affinity.

During the past year the signal-to-noise ratio of the tandem mass spectrometer has been greatly improved and the observation of protonated GeH_4 as GeH_4D^+ has been definitely confirmed. Thus, Figure 5 shows the mass spectrum obtained when D_3O^+ ions of 1.5 eV energy (laboratory system) collide with GeH_4 . The ions of principal interest in connection with protonated GeH_4 are at masses 78, 80 and 82 amu. This region of the product spectrum is shown in (b) at three times the sensitivity of (a). The possible ions that could contribute to these masses are shown in Table 7.

The absence of a peak at $m/e = 74$ amu in spectrum (a) means that $^{70}\text{GeH}_4^+$ and $^{70}\text{GeH}_2\text{D}^+$ are not produced in the reaction and therefore we may rule out $^{74}\text{GeH}_2\text{D}^+$ and $^{74}\text{GeH}_4^+$ as making a contribution to

Figure 5.

Table 7

<u>Mass</u>	<u>Possible Ions</u>
78	$^{72}\text{GeH}_4\text{D}^+$, $^{74}\text{GeH}_2\text{D}^+$, $^{74}\text{GeH}_4^+$, $^{76}\text{GeH}_2^+$
80	$^{74}\text{GeH}_4\text{D}^+$, $^{76}\text{GeH}_4^+$
82	$^{76}\text{GeH}_4\text{D}^+$

the peak at $m/e = 78$ and $^{76}\text{GeH}_4^+$ as making a contribution to $m/e = 80$. The absence of peaks at $m/e = 72$ and $m/e = 74$ means also that $^{70}\text{GeH}_2^+$ and $^{72}\text{GeH}_2^+$ are not formed and hence $^{76}\text{GeH}_2^+$ cannot be a contributor to the peak at $m/e = 78$. Thus only the deuterated GeH_4 , namely GeH_4D^+ , can be responsible for the ion-currents at $m/e = 78, 80$, and 82 and this conclusion means that the intensities of these ions must be in the ratio of the natural isotopic abundances of ^{72}Ge , ^{74}Ge and ^{76}Ge . That this is true can be seen from Table 8 in which the comparison is made. The agreement establishes the existence of GeH_4D^+ with a lower limit to the proton affinity of GeH_4 of 170 kcal/mole.

Table 8

<u>Mass (amu)</u>	<u>Ion</u>	<u>Relative Abundance of Ion</u>	<u>Relative Abundance of Ge Isotope</u>
78	$^{72}\text{GeH}_4\text{D}$	1	1
80	$^{74}\text{GeH}_4\text{D}^+$	5	4.70
82	$^{76}\text{GeH}_4\text{D}$	4	3.53

The answer to the question as to whether protonated NH_3 will transfer a proton to GeH_4 was obscured in the previous studies¹, by the probable contamination of the ND_4^+ beam with D_3O^+ , the latter ion resulting from displacement of D_2O from the walls of the ion-source. D_3O^+ and ND_4^+ have the same m/e value and cannot be distinguished in the beam.

Experiments using $^{15}\text{ND}_3$ as the source of ammonium- d_4 ions are now in progress and will circumvent the problem of displacing water from the walls, since $^{15}\text{ND}_4^+$ has an m/e value of 21 amu, as compared with 20 amu for D_3O^+ .

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6. MULTIPHOTON INFRARED DECOMPOSITION OF SILANES

A CO₂-TEA laser (Lumonics-103-2) has been obtained from Lumonics Ltd. Installation has been slower than anticipated due to an unexpected delay in new personnel joining the research group. Nonetheless, installation of the laser as a source of radiation complementary to the vacuum ultraviolet source for the photodecomposition cell in the time-of-flight mass spectrometer is nearly complete. Secondly, Dr. J. Blazejowski from the University of Gdansk in Poland will be joining the research effort on September 24, 1979 and he will devote 100% of his efforts to the infrared multiphoton decomposition of SiH₄ and Si₂H₆.

It is anticipated that infrared photodecomposition experiments will be initiated in October 1979.

PERSONNEL SUPPORTED BY DOE EY-76-S-02-3416

1. Robert N. Abernathy, B. S. California State College. Presently a Ph.D. candidate at The Pennsylvania State University.
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14. Thomas M. Mayer, Ph.D. The Pennsylvania State University, 1975. Presently a Research Chemist at Bell Laboratories, Murray Hill, New Jersey.
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ANNUAL LIST OF REPRINTS, PREPRINTS, THESES, LECTURES, ETC.

A. Reprints and Preprints

1. G. G. A. Perkins, E. R. Austin and F. W. Lampe, "The 147-Nanometer Photolysis of Monosilane," J. Am. Chem. Soc. 101, 1109 (1979).
2. G. W. Goodloe and F. W. Lampe, "The Reactions of Methyl Cations with Methylsilanes," J. Am. Chem. Soc. 101, 3472 (1979).
3. G. W. Goodloe and F. W. Lampe, "Reactions of Methyl Cations with Ethyl Silanes," J. Am. Chem. Soc. 101, xxxx (1979), In Press.
4. G. W. Goodloe and F. W. Lampe, "Reactions of Ethyl, Propyl and Butyl Cations with Methyl and Ethyl Silanes," J. Am. Chem. Soc. 101, xxxx (1979), In Press.
5. G. G. A. Perkins and F. W. Lampe, "The 147-Nanometer Photolysis of Disilane," J. Am. Chem. Soc. (Submitted).
6. G. Burns and F. W. Lampe, "On the Heteronuclear Recombination of Chlorine and Iodine Atoms," J. Phys. Chem. (Submitted).

B. Lectures

1. F. W. Lampe, "Collision Complexes in Ion-Molecule Reactions," at the NATO Advanced Study Institute on Kinetics of Ion-molecule Reactions, LaBaule, France, September 6, 1978.
2. F. W. Lampe, "The Photochemistry of Monosilane," at the Max-Planck Institute für Kohlenforschung, Mülheim, Germany, September 15, 1978.
3. F. W. Lampe, "Long-lived Collision Complexes in Ion-molecule Reactions," at the Hahn-Meitner Institut für Kernforschung, Berlin, Germany, September 18, 1978.
4. F. W. Lampe, "Long-lived Collision Complexes in Ion-Molecule Reactions," at West Virginia University, Morgantown, West Virginia, November 8, 1978.
5. F. W. Lampe, "Decomposition of Silanes in the Gas-Phase," at the T. J. Watson Research Center of IBM, Yorktown Heights, New York, November 21, 1978.
6. F. W. Lampe, "Long-lived Collision Complexes in Ion-Molecule Reactions," at The University of Toronto, Toronto, Ontario, Canada, January 12, 1979.
7. F. W. Lampe, "Ionic and Radical Reactions of Silanes," at the Faculty Seminar, The Pennsylvania State University, University Park, Pennsylvania, February 13, 1979.

8. F. W. Lampe, "Decompositions of Silanes in the Gas-Phase," at Brookhaven National Laboratory, Upton, New York, April 26, 1979.
9. F. W. Lampe, "Reactions of Alkyl Ions with Methyl Silanes," American Society of Mass Spectrometry, Seattle, Washington, June 4, 1979.
10. G. G. A. Perkins, "The 147 Nanometer Photolysis of Monosilane," Middle Atlantic Regional Meeting of the American Chemical Society, West Long Branch, New Jersey, April 1979.

C. Theses

1. George W. Goodloe, "The Ion-Molecule Reactions of Alkyl Silanes," Ph.D. Dissertation, The Pennsylvania State University, University Park, Pennsylvania, May 1979.

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