MASTER

RADIATION CHEMISTRY OF VOLATILE
SILANES AND GERMANES

Progress Report
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F. W. Lampe
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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Preface

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

A. Gamma-ray Irradiations

Radiolyses of silanes and germanes and of mixtures of these substances with noble gases, organic compounds, free-radical scavengers, and ion scavengers are conducted using a Co⁶⁰ source. The irradiations are followed by product analyses, using mass spectrometric and gas chromatographic techniques, to determine radiation yields as functions of experimental conditions. Mechanistic conclusions are drawn from the dependence of the radiation yields on reaction conditions, utilizing knowledge of pertinent elementary processes drawn from B and C below.

B. Photochemical and Photosensitized Initiation of Free-radical Reactions

Initiation of the decomposition of silanes and germanes by photosensitization and direct photolysis enables us to identify and study the purely free-radical mechanisms involved. The knowledge obtained concerning photochemical decompositions of these compounds is not only of considerable intrinsic value but is essential to an understanding of the radiation chemistry.

C. Ion-Molecule Reaction

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.

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, 1976 to August 31, 1977. During the report year most work was done with silane and organosilane systems and the emphasis was almost equally divided between A, B, and C. This report consists of abstracts of the studies carried out in the various topics during the report-year.

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1. FREE-RADICAL CHAIN FORMATION OF SILOXANES IN THE
RADIOLYSIS OF MONOSILANE-NITRIC OXIDE MIXTURES

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The irradiation of pure SiH_4 results in the formation of H_2 and Si_2H_6 with G-values of 15.2 and 7.0, respectively. Traces of higher silanes and a brown solid deposit containing silicon and hydrogen are also observed. As may be seen in Table I, the addition of NO in quantities ranging from 2% to 30% of the SiH_4 results in a reduction of the Si_2H_6 yield to a value that is 41% of that in pure SiH_4 . The fact that $G(\text{Si}_2\text{H}_6)$ is independent of NO concentration in the range of 2-30% indicates that complete suppression of Si_2H_6 formation by way of SiH_3 -radical combination has been achieved. The residual yield of Si_2H_6 must be due to reactions of SiH_3^+ ions and SiH_2 radicals, neither of which react with NO.^{1,2}

NO is consumed very rapidly, with the average $G(-\text{NO}) \approx 50$ indicating that a chain process is involved. The significant increase in $G(-\text{SiH}_4)$ and the formation of N_2O , $\text{SiH}_3\text{OSiH}_3$, $\text{SiH}_3\text{OSiH}_2\text{OSiH}_3$ and $\text{SiH}_3\text{OSiH}_2\text{OSiH}_2\text{OSiH}_3$ caused by the addition of NO suggest strongly that SiH_4 is involved in this chain reaction. The chain reaction involved is most likely that found by Kamaratos and Lampe³ in the $\text{Hg}(^3\text{P}_1)$ photosensitized decomposition of SiH_4 -NO mixtures.

On the basis of the results obtained the mechanism of the radiation-induced decomposition of SiH_4 -NO mixtures is proposed to be as shown below.

etc.

Reactions (3)-(10) comprise the chain formation of N_2O and siloxanes while (11)-(14) depict the mechanisms of Si_2H_6 formation that is not suppressible by NO.

The observation that the solid silicon hydride deposit is significantly reduced by the presence of NO suggests that this deposit is formed by SiH_3 radicals reaching the

walls of the vessel. Interest in the mechanism of formation of this solid has very recently been aroused by the newly discovered possibilities of preparing very inexpensive solar cells from such amorphous silicon.⁴

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TABLE 1
100-eV Yields in Radiolysis of SiH₄-NO Mixtures^a

Compound	G(molecules/100eV) at P(NO) in Torr					
	0	2	5	10 ^b	20	30
SiH ₄	-36±27	-	-53±18	-	-90±22	-
NO	-	-	-49±3	-39±3	-49±8	-64±10
H ₂	15.2±0.4	13±2	15.8±0.3	13±2	14±2	12.7±0.4
Si ₂ H ₆	7.0±1.0	3.0±0.9	3.0±0.1	(2.9±0.9) ^b	2.8±0.1	2.9±0.3
N ₂ O	-	-	18.5±0.8	16±1	16.3±0.8	15.4±0.5
(SiH ₃) ₂ O	-	-	12.0±0.2	7±1	7.6±0.4	4.6±0.2
(SiH ₃ O) ₂ SiH ₂	-	-	3.5±2.0	2.2±0.5	2.3±0.1	0.71±0.1
SiH ₃ (OSiH ₂) ₂ OSiH ₃	-	-	1.0±0.1	0.43±0.10	0.55±0.10	0.35±0.10

a) Pressure of SiH₄ was 100 torr in all experiments.

b) For reasons unknown, but probably related to incorrect dose rate in these experiments, the G-values of this series all appeared to be low. The values shown in this column have been corrected by the assumption that G(Si₂H₆) would have the apparent plateau value of 2.9. The multiplicative factor was 1.25.

2. RADIATION-INDUCED REACTION OF SILYL IONS WITH ETHYLENE

Mass spectrometric studies in this laboratory^{1,2} have shown that SiH_3^+ ions react with C_2H_4 to form the $\text{C}_2\text{H}_5\text{SiH}_2^+$ ion. Moreover, the $\text{C}_2\text{H}_5\text{SiH}_2^+$ ions, so formed, will react successively with two more molecules of C_2H_4 to form the $(\text{C}_2\text{H}_5)\text{SiH}^+$ and $(\text{C}_2\text{H}_5)_3\text{Si}^+$ ions.¹ Addition of a fourth C_2H_4 molecule could not be detected. The occurrence of such ion-molecule reactions in a γ -ray irradiation should be detectable in terms of ethylsilane products provided the formation of these products by reactions of SiH_3 radicals with C_2H_4 ^{3,4} is prevented. Accordingly we have studied the radiation chemistry of SiH_4 - C_2H_4 mixtures in which NO is present at a level of 5%. Previous work⁵ has shown that 5% of NO completely scavenges SiH_3 radicals.

Typical results are shown in Figures 1 and 2 in which concentrations of reactants and products are plotted as functions of total energy absorbed. The 100-eV yields are shown in Table II.

It is apparent from Table II that, as expected, the system is much more complex than when C_2H_4 is absent. Nonetheless it is clear that $\text{C}_2\text{H}_5\text{SiH}_3$ is not a product of the irradiation of an equimolar mixture of C_2H_4 and SiH_4 with NO present, although it is a major product in the absence of NO.^{3,4} $(\text{C}_2\text{H}_5)_2\text{SiH}_2$ is also not formed in the present system. However, significant yields of $(\text{C}_2\text{H}_5)_3\text{SiH}$ are

obtained and on the basis of our mass-spectrometric studies we propose the mechanism to be

The yield of Si_2H_6 is reduced from the value observed in the SiH_4 -NO system. This is to be attributed to competition of SiH_4 and C_2H_4 for SiH_3^+ -ions. If it is assumed that the reaction

is always followed by reaction of Si_2H_7^+ with SiH_4 to form Si_2H_6 , then a straight-forward, steady-state kinetic treatment of reactions (1)-(5) leads to the conclusion

$$\frac{G[(\text{C}_2\text{H}_5)_3\text{SiH}]}{G(\text{Si}_2\text{H}_6)} = \frac{k_1[\text{C}_2\text{H}_4]}{k_5[\text{SiH}_4]} \quad (6)$$

A plot of the experimental data according to (6) is shown in Figure 3. The linearity of the plot and the fact that the line passes naturally through the origin, as required by (6), is confirming evidence of the validity of the mechanism (1)-(5). The slope of the line in Figure 3 is 0.14, which indicates that SiH_3^+ add to SiH_4 seven times faster than they add to C_2H_4 .

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Table II

100 eV Yields in γ -Radiolysis of an Equimolar SiH_4 - C_2H_4
Mixture with 5% NO

<u>Species</u>	<u>$G(\frac{\text{molecules}}{100 \text{ eV}})$</u>	<u>Species</u>	<u>$G(\frac{\text{molecules}}{100 \text{ eV}})$</u>
SiH_4	-40 ± 16	N_2	10.7 ± 4
NO	-38 ± 4	$\text{SiH}_3\text{OSiH}_3$	0.35 ± 0.1
C_2H_4	-38 ± 15	$\text{SiH}_3\text{OSiH}_2\text{OSiH}_3$	-
H_2	14.6 ± 0.8	$\text{C}_2\text{H}_5\text{SiH}_3$	-
Si_2H_6	0.77 ± 0.10	$(\text{C}_2\text{H}_5)_2\text{SiH}_2$	-
N_2O	4.6 ± 0.1	$(\text{C}_2\text{H}_5)_3\text{SiH}$	0.11 ± 0.03

Figure 1. Dependence of Reactant and Product Concentrations on Dose in the Gamma-Radiolysis of a SiH₄-NO-C₂H₄ Mixture (75 torr SiH₄, 7.5 torr C₂H₄).

Figure 2. Dependence of Product Concentrations on Dose in the Gamma-Radiolysis of a SiH₄-NO-C₂H₄ Mixture (75 torr SiH₄, 7.5 torr NO, 75 torr C₂H₄).

Figure 3. Relative Yields of $(C_2H_5)_3SiH$ and Si_2H_6 as a Function of $[C_2H_4]/[SiH_4]$.

3. RATE CONSTANTS FOR THE REACTIONS OF HYDROGEN ATOMS WITH METHYL GERMANES

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Existing kinetic information concerning the reactions of hydrogen atoms and other free radicals with alkyl germanes is very meager^{1,2} and no such data exists for alkyl germanes which contain at least one Ge-H bond. Recently we² have developed a mass spectrometric technique to measure rate constants for the reactions of hydrogen atoms with a variety of substrate molecules and during the report year we have applied this technique to the reactions of hydrogen atoms with the methyl germanes.

Hydrogen atoms were generated by $\text{Hg}(^3\text{P}_1)$ photosensitization of hydrogen-substrate mixtures which contained about 98% hydrogen. 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. As we have shown,² measurement of the initial rate of decrease of an ion-current arising from the methyl germane relative to the initial rate of decrease of an ion-current from an internal standard leads directly to the ratio $\frac{k_1}{k_2}$ that pertains to the reactions

Since k_2 is known,^{2,3} k_1 is easily calculated. Disilane was used as the internal standard because it has a convenient rate of H-atom induced decomposition and the ionic masses arising from its decomposition products do not interfere with the masses of the ions from the methyl germanes.

The results of our measurements are given in Table III in terms of the ratio $\frac{k_1}{k_2}$ and the absolute value of k_1 , determined using $k_2 = 3.7 \pm 0.6 \times 10^{-12} \text{ cm}^3/\text{sec.}^2$ Also given in Table III are the m/e values of the ions used in the mass spectrometric monitoring of the $\text{Me}_n\text{GeH}_{4-n}$ concentration and the number of replicate measurements involved in determining each value. The ion of $m/e = 62$ was used to monitor Si_2H_6 concentration. The upper limit to the value for Me_4Ge was not determined experimentally, but is assumed on the basis of the experimental studies made on Me_4Si^2 and Me_4Sn , i.e., there was no measurable reaction within the uncertainty of our measurements. Since Ge lies between Si and Sn in Group IV of the periodic table, it would be very surprising if Me_4Ge reacted at a measurable rate.

Comparison of the rate constants for hydrogen-atom induced decomposition of the methyl germanes with those of the methyl silanes² shows that hydrogen atoms react faster with the methyl germanes by factors of 5-6. Also while methyl-substituted silanes and germanes react with hydrogen atoms faster than do monosilane or monogermane, respectively, the effect of methyl substitution on reactivity is greater in the germanes than in the silanes.

Arrhenius parameters for k_1 have been estimated by making the following assumptions:

(1) It is assumed that the pre-exponential factor for H-atom reaction with GeH_4 is the same as that for H-atom reaction with SiH_4 . This assumption is supported by the similarity of the bond lengths in these two molecules, i.e. $1.48\text{\AA}$ for the Si-H bond length in SiH_4 and $1.52\text{\AA}$ for the Ge-H bond length in GeH_4 .

(2) It is assumed that the pre-exponential factors per Ge-H bond are constant over the series $(\text{CH}_3)_n\text{GeH}_{4-n}$ with $n=0,1,2,3$. This assumption is supported by the observation that for the reaction of CH_3 -radicals with $(\text{CH}_3)_n\text{SiH}_{4-n}$ with $n=0,1,2,3$ the pre-exponential factors per Si-H bond are remarkably constant at $9.0 \pm 1.1 \times 10^{-13} \text{ cm}^3/\text{sec}.$ ⁴ We expect the germanes to be analogous to the silanes.

The Arrhenius parameters A and E ($k=Ae^{-E/RT}$) that are obtained for the series of germanes by this admittedly crude approximation are given in Table IV. It is to be noted from Table IV that the activation energies fall off slowly as the Ge-H bonds in GeH_4 are successively replaced by Ge- CH_3 bonds.

Also shown in Table IV are dissociation energies of Ge-H bonds that have been estimated using the data in Table III and the bond-energy-bond-order (BEBO) semi-empirical relationships.⁵

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TABLE III

Rate Constants for H-Atom Induced Decomposition at 32°C

<u>Substrate</u>	<u>m/e</u>	<u>No. of Runs</u>	$\frac{k_1}{k_2}$	$k_1(\text{cm}^3/\text{sec}) \times 10^{12}$
CH_3GeH_3	74	11	0.84 ± 0.08	3.1 ± 0.6
$(\text{CH}_3)_2\text{GeH}_2$	90	11	0.90 ± 0.06	3.3 ± 0.6
$(\text{CH}_3)_3\text{GeH}$	105	11	1.22 ± 0.07	4.5 ± 0.7
$(\text{CH}_3)_4\text{Si}$	88	1		< 0.01
$(\text{CH}_3)_4\text{Ge}$				< 0.01
$(\text{CH}_3)_4\text{Sn}$	165	2		< 0.01

TABLE IV

Arrhenius Parameters for H-Atom Induced Decomposition of Germanes
and Dissociation Energies of Germanium-Hydrogen Bonds

<u>Molecule</u>	<u>$A \times 10^{11} (\text{cm}^3/\text{sec})$</u>	<u>$E (\text{kcal/mole})$</u>	<u>$D(\equiv \text{Ge-H}) \text{ kcal/mole}$</u>
GeH_4^*	2.7	1.6	89
CH_3GeH_3	2.0	1.1	83
$(\text{CH}_3)_2\text{GeH}_2$	1.4	0.86	79
$(\text{CH}_3)_3\text{GeH}$	0.7	0.26	63

* The values given for GeH_4 are from Reference 2.

4. THE PHOTOCHEMICAL DECOMPOSITION OF MONOSILANE BY 147-NANOMETER RADIATION

The $\text{Hg}(^3\text{P}_1)$ photosensitized decomposition of monosilane has been studied.¹⁻⁴ The products of the reaction are H_2 , Si_2H_6 and an amorphous silicon hydride solid and the reaction appears to proceed predominantly through the formation and reaction of the monovalent SiH_3 radicals. The direct photolysis of SiH_4 has, however, not yet been reported and as part of our program of study of radiation-induced silane decomposition mechanisms we have undertaken this investigation.

The photolyses are carried out in a cylindrical cell containing a LiF window at one end and at the other end a small pinhole leading into the ion-source of a time-of-flight mass spectrometer. Starting with a freshly cleaned window, an actinometer gas is photolyzed to determine the light intensity incident on the contents of the cell. The cell is pumped out, the He-SiH_4 mixture added and photolyzed for 2-3 minutes. Such alternate photolyses of actinometer gas and He-SiH_4 is repeated until the buildup of amorphous solid on the walls has become sufficiently large that the light intensity within the cell is reduced to $\sim \frac{1}{10}$ of the value observed for a freshly cleaned window. The rate of absorption of photons is determined from the initial rate of disappearance of actinometer gas, which in turn is obtained from the initial rate of decrease of m/e 44 (N_2O^+ or CO_2^+). The initial rate of loss of SiH_4 is determined from the initial rate of decrease of m/e 31 (SiH_3^+).

The direct photochemical decomposition of SiH_4 can occur only with light of wavelength less than 165-nanometers.⁵ In our studies of the vacuum-ultraviolet photochemistry of SiH_4 we are using a xenon resonance lamp. The intensity emitted by the lamp is 2.3×10^{15} quanta/sec of which 98% is at 147 monometers. All our experiments have been conducted at a total pressure of 40 torr using He as a diluent gas. The following facts have been discovered:

1. The quantum yield for the decomposition of both SiH_4 and SiD_4 is 4.0 ± 0.2 and is independent of SiH_4 partial pressure in the range of 1-8 torr. The quantum yield of Si_2H_6 formation is 1.2 at a partial pressure of SiH_4 of 1.5 torr. The quantum yield of H_2 was not measured but, in view of the stoichiometry, is probably at least one-half of the quantum yield for SiH_4 decomposition.

2. The build-up of amorphous silicon hydride on the window drastically reduces the intensity of light transmitted by the window. However, the quantum yield of SiH_4 decomposition is independent of the amount of amorphous solid deposited. The products of the photolysis may not be independent of the amount of solid deposited, however, since it absorbs appreciable light.

3. The addition of NO, a substance that scavenges SiH_3 radicals^{3,4} but not SiH_2 radicals,⁶ shows, that at complete scavenging of SiH_3 radicals, the Si_2H_6 quantum yield

is reduced to 0.6. This is one-half of the value found in the absence of NO.

The most likely mechanism that is in accord with these experimental facts is as follows:

From this mechanism $\phi(-\text{SiH}_4) = 4$. The quantum yield of Si_2H_6 is predicted to be $2-f$, where f is the fraction of the SiH_3 radicals that undergo (5). The experimental value of $\phi(\text{Si}_2\text{H}_6) = 1.2$ indicates that 80% of the SiH_3 radicals react with the wall and produce amorphous silicon hydride.

$\phi(\text{H}_2)$ is predicted to be $2+f$, which from the experimental value of $\phi(\text{Si}_2\text{H}_6)$ becomes 2.8.

NO reacts efficiently with SiH_3 in the presence of SiH_4 to form N_2O , H_2 and $\text{SiH}_3(\text{OSiH}_2)_n\text{OSiH}_3$ with $n=0,1,2$.⁴ This means that (3) and (5) should be largely prevented, resulting in a reduction of $\phi(\text{Si}_2\text{H}_6)$ by a factor of 2 and a reduction in the amount of amorphous solid. The reduction of $\phi(\text{Si}_2\text{H}_6)$ from 1.2 to 0.6 has been observed experimentally and there are indications that the presence of NO reduces the buildup of the solid.

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5. PERSISTENT, ENERGY-RICH COLLISION COMPLEXES IN
THE REACTION OF SILYL IONS WITH ETHYLENE

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October 12th Issue (1977).

The reaction of SiH_3^+ with C_2H_4 has been studied in a tandem mass spectrometer at relative kinetic energies in the range of 0.47 to 2.4 eV and at C_2H_4 pressures in the range of 2 to 80×10^{-4} torr. The intensities of the reaction products, at several relative energies and a C_2H_4 -pressure of 5×10^{-4} torr, are shown in Table V. Of particular interest is the detection of the SiC_2H_7^+ ion at these low pressures, since this product is the simple collision adduct of the reaction

and therefore must be energy-rich. Extrapolations of the relative abundance of SiC_2H_7^+ ions to zero pressure prove that, at the lowest energies of 0.47 and 0.94 eV appreciable amounts of the energy-rich collision complexes which have not undergone stabilization are observed.

Collisional stabilization by C_2H_4 increases the relative yield of SiC_2H_7^+ so that at 80×10^{-4} torr this ion accounts for about 80% of the observed products. The other observed ionic products, namely SiC_2H_5^+ , SiC_2H_3^+ and SiCH_3^+ , arise from unimolecular breakdown of $\text{SiC}_2\text{H}_7^{+*}$. Therefore, the

relative yields of these products decrease with increasing pressure of C_2H_4 , because of collisional stabilization of $SiC_2H_7^{+*}$, and increase with increasing collision energy because of the reduced lifetime of the energy-rich collision complex. In addition, about 10% of the formation of $SiCH_3^+$, in the limit of zero pressure, is due to a direct process. The reaction mechanism is therefore concluded to consist of (1) and the following:

Reaction (3) accounts for about 90% of the break-down of $SiC_2H_7^{+*}$.

The experimental data yield absolute values for the lifetime of the energy-rich collision complexes, for the unimolecular rate constants of decomposition of the complex and for the rate constants for the single-collision stabilization of the complex. Results are shown in Table VI. Single-collision stabilization (i.e. strong collisions) is indicated by the data to be no longer possible at relative energies of reactants of 1.4 eV and above. This breakdown of the strong collision assumption leads to a

value of 0.7-1.1 eV as the maximum energy that may be transferred from $\text{SiC}_2\text{H}_7^{+*}$ to C_2H_4 in a single collision.

Rice-Ramsberger-Kassel-Marcus (RRKM) type calculations, based on the chemically activated species leading to products being the $\text{CH}_3\text{CH}_2\text{SiH}_2^{+*}$ ion, and in which angular momentum is conserved (approximately), give order-of-magnitude agreement with experiment.

The potential energy profile of the reaction, suggested by the data, is shown in Figure 4.

TABLE V

Dependence of Ion-Intensity on Collision Energy at 5×10^{-4} Torr

$\left(\frac{m}{e}\right)$	Ion	Multiplier Current in amperes $\times 10^{14}$ at Collision Energy of				
		0.47eV	0.94eV	1.4eV	1.9eV	2.4eV
31	SiH_3^+	4.65×10^4	9.97×10^4	1.72×10^5	1.99×10^5	$2.25^5 \times 10^5$
43	SiCH_3^+	21	22	30	39	60
55	SiC_2H_3^+	10	16	30	44	69
57	SiC_2H_5^+	58	101	158	170	167
59	SiC_2H_7^+	48	30	21	6	-

TABLE VI

Experimental Lifetimes and Rate Constants

<u>Collision Energy (eV)</u>	<u>$\tau \times 10^6 (\text{sec})$</u>	<u>$k_3(E^*) \times 10^{-5} (\text{sec}^{-1})$</u>	<u>$k_5(E^*) \times 10^{-4} (\text{sec}^{-1})$</u>	<u>$k_6 \times 10^9 (\text{cm}^3/\text{sec})$</u>
0.47	7.6 $\pm$ 1.6	1.1 $\pm$ 0.2	2.0 $\pm$ 0.4	2.5 $\pm$ 0.4
0.94	4.4 $\pm$ 1.9	2.0 $\pm$ 0.8	2.7 $\pm$ 1.2	3.3 $\pm$ 0.4

Figure 4.

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

1. William N. Allen, Ph.D. The Pennsylvania State University, 1977. Presently a Research Associate at the Naval Research Laboratory, Washington, D. C.
2. Ernest R. Austin, Ph.D. The Pennsylvania State University, 1977. Presently a Post-doctoral Assistant at the Pennsylvania State University.
3. John P. Bare, Ph.D. The Pennsylvania State University, 1977. Presently a Research Chemist at the Dupont Company, Wilmington, Delaware.
4. David P. Beggs, Ph.D. The Pennsylvania State University, 1969. Presently a Senior Scientist at Hewlett Packard Company, Avondale, Pennsylvania.
5. T. M. H. Cheng, Ph.D. University of California. Presently a Senior Chemist at General Aniline and Film Corporation, Wayne, New Jersey.
6. George W. Goodloe, B. S. Brooklyn Polytechnic Institute. Presently a Ph.D. candidate at The Pennsylvania State University.
7. George G. Hess, Ph.D. The Pennsylvania State University, 1965. Presently Professor of Chemistry at Wright State University, Dayton, Ohio.
8. E. Kamaratos, Ph.D. The Pennsylvania State University, 1969. Presently Research Associate at University of Washington, Seattle, Washington.
9. V. Kempster, Ph.D. University of Freiburg. Presently Research Associate at University of Freiburg, Freiburg, Germany.
10. Herbert N. Maier, Ph.D. The Pennsylvania State University, 1971. Presently Laboratory Director at Precision Gas Products, Inc., Rahway, New Jersey.
11. Thomas M. Mayer, Ph.D. The Pennsylvania State University, 1975. Presently a Research Chemist at Bell Laboratories, Murray Hill, New Jersey.
12. Joanne K. Northrup, M. S. The Pennsylvania State University, 1972. Presently a Ph.D. student at University of Chicago, Chicago, Illinois.

13. George G. A. Perkins, B. S. St. John's University, Jamaica, New York. Presently a Ph.D. candidate at The Pennsylvania State University.
14. Peter Potzinger, Ph.D. University of Graz. Presently a Group Leader at Max-Planck Institute for Carbon-Research, Mülheim, Germany.
15. John F. Schmidt, Ph.D. The Pennsylvania State University. Presently Professor of Chemistry at Shepherd College, Shepherdstown, West Virginia.
16. Hiok-Seng Tan, Ph.D. The Pennsylvania State University, 1972. Presently Research Chemist with a chemical company in Singapore.
17. Tung-Yang Yu, Ph.D. The Pennsylvania State University, 1972. Presently Research Associate at Wright-Patterson Air Force Base, Dayton, Ohio.
18. John R. Krause, Ph.D. University of Western Ontario. Presently an Instructor at the University of Ottawa, Ottawa, Ontario, Canada.

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

1. E. R. Austin and F. W. Lampe, "Hydrogen-Atom Initiated Decomposition of Monosilane," J. Phys. Chem., 80, 2811 (1976).
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., 65, 3378 (1976).
3. R. D. Smith, J. J. DeCorpo, W. N. Allen and F. W. Lampe, "Complex Formation in the $\text{C}^+(2\text{P}) + \text{CH}_4$ Reaction at 0.1 to 10 eV." J. Chem., 65, 3665 (1976).
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., 98, 7826 (1976).
5. J. R. Krause and F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-CF}_4$ Mixtures," J. Phys. Chem. 81, 281 (1977).
6. W. N. Allen and F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-C}_6\text{H}_6$ Mixtures," J. Am. Chem. Soc., 99, 2943 (1977).
7. W. N. Allen, T. M. H. Cheng, F. W. Lampe, "Ion-Molecule Reactions in $\text{SiH}_4\text{-D}_2$ Mixtures," J. Chem. Phys., 66, 3371 (1977).
8. F. W. Lampe, T. H. Risby and F. A. Serravallo, "Steady-state Kinetic Treatment of the Emission from Reduced-Pressure, Microwave-induced Discharges in Helium," Anal. Chem., 49, 560 (1977).
9. E. R. Austin and F. W. Lampe, "Rate Constants for the Reactions of H-Atoms with Silanes and Germanes," J. Phys. Chem. 81, 1134 (1977).
10. J. P. Bare and F. W. Lampe, "Free-radical Chain Formation of Siloxanes in the Radiolysis of $\text{SiH}_4\text{-NO}$ Mixtures," J. Phys. Chem. 81, 1437 (1977).
11. E. R. Austin and F. W. Lampe, "Rate Constants for the Reactions of H-Atoms with Methylgermanes," J. Phys. Chem., 81, 1546 (1977).
12. W. N. Allen and F. W. Lampe, "Persistent Collision Complexes in the Reaction of Silyl Ions with Ethylene," J. Am. Chem. Soc., 99, To appear in the October 12th issue (1977).

B. Lectures

1. W. N. Allen, "Persistent Collision Complexes in the Reactions of Silyl Ions with Ethylene," American Society of Mass Spectrometry Meeting, Washington, D.C., May 31, 1977.
2. F. W. Lampe, "Ion-Molecule Reactions and Mass Spectrometry," At Department of Chemistry, Geneva College, Beaver Falls, Pennsylvania, November 19, 1976.
3. F. W. Lampe, "Rate Constants for Reactions of H-Atoms with Silanes and Germanes," American Chemical Society Meeting, New Orleans, Louisiana, March 23, 1977.
4. F. W. Lampe, "Persistent Collision Complexes in Ion-Molecule Reactions," Department of Chemistry, University of Kansas, Lawrence, Kansas, March 24, 1977.
5. F. W. Lampe, "Persistent Collision Complexes in the Reactions of Silyl Ions," Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, April 18, 1977.
6. F. W. Lampe, "Persistent Collision Complexes in the Reactions of Silyl Ions with Benzene," American Society of Mass Spectrometry Meeting, Washington, D.C., May 31, 1977.

C. Theses

1. W. N. Allen, "Ion-Molecule Reactions in Silane Systems," Ph.D. Thesis to the Graduate School of The Pennsylvania State University, January 28, 1977.
2. E. R. Austin, Jr., "A Mass-Spectrometric Study of the Hydrogen Atom Induced Decomposition of Silanes and Germanes," Ph.D. Thesis to the Graduate School of The Pennsylvania State University, April 22, 1977.
3. J. P. Bare, "The Gamma Radiolysis of Silane-Nitric Oxide and Silane-Nitric Oxide-Ethylene Mixtures," Ph.D. Thesis to the Graduate School of The Pennsylvania State University, August 29, 1977.

PUBLICATIONS LIST FROM ERDA CONTRACT EY-76-S-02-3416

1. G. G. Hess and F. W. Lampe, "Ionic Reactions in Gaseous Monosilane," J. Chem. Phys. 44, 2257 (1966).
2. "Energetic Properties of Group IV Hydrides and Their Alkyl Derivatives by Electron Impact," G. G. Hess, F. W. Lampe, and A. L. Yergey, Ann. N. Y. Acad. Sci. 136, 106 (1966).
3. D. P. Beggs and F. W. Lampe, " SiH_5^+ Formation in Ionized CH_4 - SiH_4 Mixtures," J. Chem. Phys. 49, 4230 (1968).
4. J. F. Schmidt and F. W. Lampe, "Gamma-Ray Radiolysis of Silane and Silane-Ethylene Mixtures," J. Phys. Chem. 73, 2706 (1969).
5. D. P. Beggs and F. W. Lampe, "Ionic Reactions in SiH_4 - C_2H_2 Mixtures," J. Phys. Chem. 73, 3307 (1969).
6. D. P. Beggs and F. W. Lampe, "Ionic Reactions in SiH_4 - C_2H_4 Mixtures," J. Phys. Chem. 73, 3315 (1969).
7. P. Potzinger and F. W. Lampe, "Ionization and Dissociation in SiH_4 and Si_2H_6 ," J. Phys. Chem. 73, 3912 (1969).
8. D. P. Beggs and F. W. Lampe, "Ionic Reactions in SiH_4 - CH_4 and SiH_4 - C_6H_6 Mixtures," J. Phys. Chem. 73, 4194 (1969).
9. P. Potzinger and F. W. Lampe, "Ionic Reactions in CH_3SiH_3 ," J. Phys. Chem. 74, 587 (1970).
10. P. Potzinger and F. W. Lampe, "Thermochemistry of Simple Alkylsilanes," J. Phys. Chem. 74, 719 (1970).
11. E. Kamaratos and F. W. Lampe, "Mass-Spectrometric Studies of the Mercury Photosensitized Reactions of SiH_4 and CH_3SiH_3 with NO ," J. Phys. Chem. 74, 2267 (1970).
12. P. Potzinger and F. W. Lampe, "Ion-Molecule Reactions in $(\text{CH}_3)_2\text{SiH}_2$, $(\text{CH}_3)_3\text{SiH}$ and $(\text{CH}_3)_4\text{Si}$," J. Phys. Chem. 75, 13 (1971).
13. Tung-Yang Yu, T. M. H. Cheng, V. Kempter and F. W. Lampe, "Ionic Reactions in Monosilane. Radiation Chemistry Implications," J. Phys. Chem. 76, 3321 (1972).
14. Hiok-Seng Tan and F. W. Lampe, "Reactions of Ethyl Radicals with Nitric Oxide. Nitrosoethane and Triethylhydroxylamine," J. Phys. Chem. 76, 3303 (1972).

15. Joanne K. Northrup and F. W. Lampe, "Ionic Reaction in Gaseous Monogermene," J. Phys. Chem. 77, 30 (1973).
16. T. M. H. Cheng and F. W. Lampe, " SiH_5^+ and the Proton Affinity of SiH_4 ," Chem. Phys. Letts. 19, 532 (1973).
17. Hiok-Seng Tan and F. W. Lampe, "Mass-Spectrometric Study of the Reactions of Trifluoromethyl Radicals with Nitric Oxide," J. Phys. Chem. 77, 1335 (1973).
18. T. M. H. Cheng, Tung-Yang Yu, and F. W. Lampe, "Ion-Molecule Reactions in Monosilane-Methane Mixtures," J. Phys. Chem. 77, 2587 (1973).
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24. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Monosilane-Ethylene Mixtures," J. Phys. Chem. 78, 2433 (1974).
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26. F. W. Lampe, "Ion-Molecule Reactions in Silane and Organosilane Systems," INTERACTION BETWEEN IONS AND MOLECULES. (P. Ausloos, Ed.), Plenum Publishing Corporation, New York, New York, 1975.
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35. F. W. Lampe, T. H. Risby, and F. A. Serravallo, "Steady-state Kinetic Treatment of the Emission from Reduced-Pressure, Microwave-Induced Discharges in Helium," Anal. Chem. 49, 560 (1977).
36. E. R. Austin and F. W. Lampe, "Rate Constants for the Reactions of H-Atoms with Silanes and Germanes," J. Phys. Chem. 81, 1134 (1977).
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