

RADIATION CHEMISTRY AND MASS SPECTROMETRY OF
VOLATILE SILANES AND GERMANES

Progress Report

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Preface

Our continuing study of the 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. Mass-spectrometric 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 and of the purely ionic component of a chemical conversion initiated by ionizing radiation.
- C. Mass-spectrometric 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 photosensitization so that ionization of the systems does not occur and we may study the pertinent free-radical reactions independently of the ionic processes.

This annual progress report describes work done from June 1, 1973 to May 31, 1974. In any program of such a nature 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. During the report year all work was done with volatile silane systems and while the emphasis was almost equally divided between A, B, and C above, most progress was made in area B.

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This report consists of abstracts of the various topics in this program studied during the report-year. Reprints from the scientific literature that describe completed topics in this program, including earlier reprints that were not available at the time of the last progress report, accompany the progress report as a separately bound appendix.

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1. POSITIVE-ION REACTIONS IN MONOSILANE-WATER MIXTURES¹

(COO-3416-9)

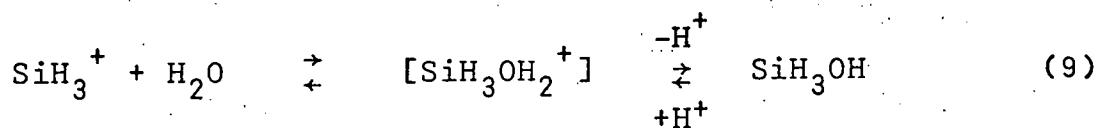
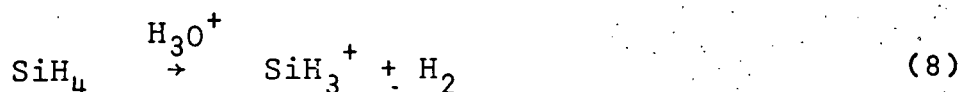
A direct correspondence has been shown to exist between the ion-molecule reactions of central importance in the radiation chemistry of gaseous methane and those characteristic of very strong acid solutions of methane.^{2,3} It has been known for over 50 years⁴⁻⁶ that monosilane reacts with water under alkaline or acid conditions to yield, ultimately, hydrogen in amounts equal to twice that contained in the monosilane. While the overall reaction is thought to proceed via silanol and disiloxane intermediates, little is known or has been done since the pioneering researches of Alfred Stock and his collaborators.⁴⁻⁷ However, the necessity of having alkaline or acidic conditions indicates that ionic reactions are of importance, and indeed one might expect, by analogy with methane, that some of the ionic processes involved are also of central importance in the radiation chemistry of monosilane-water systems. Accordingly we have conducted a mass spectrometric studies of the ion-molecule reactions occurring in this system.

The principal bimolecular reactions found and their rate constants at ambient temperature are shown in the table below:

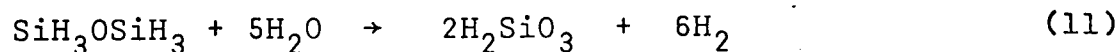
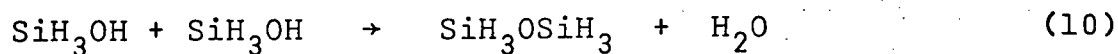
Reaction No.	Reaction	$k \times 10^{10} \text{ cm}^3/\text{sec}$
1.	$\text{H}_2\text{O}^+ + \text{SiH}_4 \rightarrow \text{H}_3\text{O}^+ + \text{SiH}_3$	0.79 ± 0.10
2.	$\text{H}_2\text{O}^+ + \text{SiH}_4 \rightarrow \text{SiH}_2^+ + \text{H}_2\text{O} + \text{H}_2$	1.9 ± 0.3
3.	$\text{H}_2\text{O}^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{H}_2\text{O} + \text{H}$	2.1 ± 0.3
4.	$\text{H}_3\text{O}^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{H}_2\text{O} + \text{H}_2$	$\geq 1.1 \pm 0.2$

Reaction No.	Reaction	$k \times 10^{10} \text{ cm}^3/\text{sec}$
5	$\text{H}_3\text{O}^+ + \text{SiH}_4 \rightarrow \text{SiH}_5^+ + \text{H}_2\text{O}$	$>0.19 \pm 0.03$
6	$\text{SiH}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SiOH}^+ + \text{H}_2$	0.058 ± 0.008

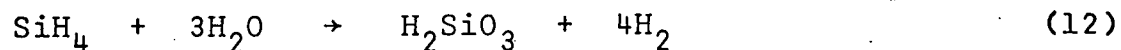
Since gaseous monosilane is a stronger base than methane, in both the Bronsted and Lewis concepts,⁸⁻¹⁰ we suggest that a carry-over to the solution phase of this relative base strength is the reason that monosilane is decomposed even in aqueous acids while much stronger acids are required to induce decomposition of methane. On the basis of our results and by analogy with the Olah mechanism describing the behavior of methane in very strong acids^{2,3} we propose the long-known⁴⁻⁶ acid hydrolysis of monosilane to occur by the following mechanism:



Further decomposition proceeds via reaction of SiH_3OH by unknown mechanisms to produce disiloxane, silicic acid and hydrogen, viz.



with the net stoichiometry of the decomposition being



With regard to gas-phase radiation chemistry of monosilane-water mixtures, (1)-(3) in the table will be of importance in monosilane-rich systems with the ionic products of (1) and (2) reacting further principally to yield SiH_3^+ . This latter ion will then react with monosilane to yield mainly disilane or with water via (6). At sufficiently high pressures (>0.1 torr) the intermediate of (6), namely $\text{SiH}_3\text{OH}_2^+$ is stabilized by collision as shown in (9). In water-rich mixtures, reaction (4)-(6) will dominate but the major overall reaction should be essentially unchanged.

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2. ION-MOLECULE REACTIONS IN DISILANE¹

(COO-3416-12)

At the beginning of the report year, the high-pressure mass-spectrometric studies in the single-source instrument had been completed but detailed interpretation awaited a study of reaction identification using tandem mass spectrometry.

From the point of view of ion-molecule reactions, disilane exhibits an extremely complex behavior. All primary ions of disilane, namely SiH_x^+ ($x=0, 1, 2, 3$) and Si_2H_x ($x=0, 1, 2, \dots, 6$), are of significant intensity and react with Si_2H_6 molecules, with over 35 exothermic reactions being unambiguously identified. Rate constants have been determined for all exothermic reactions. In addition, numerous endothermic reactions were identified. The total rate constants for depletion of Si^+ , SiH^+ , SiH_2^+ , and SiH_3^+ are in the range of 0.5-0.8 of the Langevin orbiting-encounter rate constant;² the rate constants measured for depletion of disilicon-ions are somewhat lower, probably because we were unable to measure disiliconium ion products from disilicon-ion reactants and the rate constants of any such reactions are not included in the total reactions of each reactant ion.

In addition to reflecting the consequences of all the exothermic bimolecular reactions identified in the tandem mass-spectrometric studies, the single-source pressure dependence experiments, carried out to 0.2 torr, showed numerous tertiary and higher-order processes. In fact, it is clear that the principal chemical result of ionizing disilane at pressures above 0.1 torr is to initiate a gas-phase ionic polymerization to higher silicon hydrides that is carried mainly by $Si_nH_{3n-2}^+$, $Si_nH_{2n}^+$, $Si_nH_{2n+1}^+$, and $Si_nH_{2n+3}^+$ ions. Also produced as by-products of this polymerization are SiH_4 and H_2 .

These results suggest that the radiolysis of disilane would be strongly influenced by this polymerization and formation of SiH_4 and H_2 . A recent report³ of the reactions of Si_2H_5 , SiH_3 and H with Si_2H_6 demonstrates also that the free-radical paths initiated in the radiolysis lead also the H_2 , SiH_4 , and higher silicon hydrides including Si_3H_8 and Si_4H_{10} . Radiolysis of disilane has not yet been carried out.

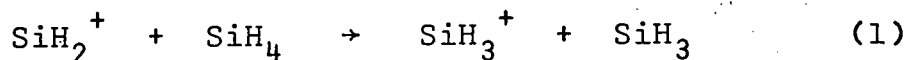
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3. KINEMATICS OF HYDRIDE-ION AND HYDROGEN-ATOM TRANSFER REACTIONS IN MONOSILANE¹

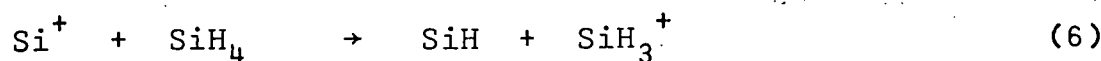
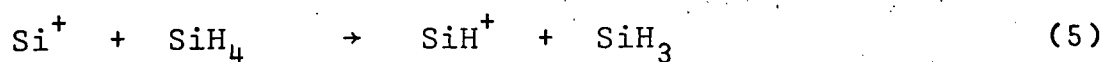
(COO-3416-13)

Reactions whose overall chemistry can be described as the transfer of a hydride-ion from a neutral molecule to an attacking positive ion are known to be of particular importance in the gas-phase chemistry of ionized silanes²⁻⁶ and mixtures of silanes with simple organic molecules.⁷⁻¹¹ However, little or no detailed knowledge of the mechanistic nature of these hydride-ion transfer reactions has been presented to date, and indeed, such as important reaction as (1), viz.



can be described equally well as either a hydride-ion transfer reaction or a hydrogen-atom transfer process.

During the report year we studied the kinematics of (1) and the following reactions in monosilane in a tandem mass spectrometer using kinetic energy analysis of mass-separated product ions that are scattered in the forward direction:



Reactions involving net hydride-ion transfer, namely (1), (2), (4), and (6) were found to proceed via a direct, stripping type

process¹² yielding SiH_3^+ products with very little kinetic energy and also via a reaction complex that is particularly prominent at lower collision energies. Direct H-atom transfer processes are observed in reactions (1), (3), and (5) and approach the predictions of the spectator stripping model at high collision energies (above 4 eV center-of-mass).

For those cases in which direct mechanisms and intermediate complex mechanisms yield the same product ion, it was found that the two types of channel proceed with nearly equal cross-sections at low collision energies. At higher collision energies the direct mechanisms completely dominate the reaction.

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4. ION-MOLECULE REACTIONS IN MONOSILANE-ACETYLENE MIXTURES¹

(COO-3416-14)

Several years ago we reported rate constants for a number of ion-molecule reactions identified in $\text{SiH}_4\text{-C}_2\text{H}_2$ mixtures.² In this study, which was carried out in a single-source mass spectrometer, reaction identification was made principally on the basis of appearance potential measurements of product ions and rate constants were determined by the pulsed-source technique³ at ion-source pressures below 0.006 torr. Since application of the same apparatus and techniques to the $\text{SiH}_4\text{-CH}_4$ system has been shown by more refined techniques^{4,5} to have yielded incomplete and/or misleading results, a reinvestigation of the $\text{SiH}_4\text{-C}_2\text{H}_2$ system was felt to be necessary. Accordingly during the report year we have carried out a tandem and high-pressure (up to 0.3 torr) investigation of the ion-molecule reactions characteristic of this system.

The reactions identified for the major primary ions in a mono-silane-rich mixture and the phenomenological rate constants determined for 1.4 eV kinetic energy (LAB) ions are shown in the table below.

Reaction	$k \times 10^{10} (\text{cm}^3\text{-sec}^{-1})$
$\text{C}_2\text{H}_2^+ + \text{SiH}_4 \rightarrow \text{Si}^+ + \text{C}_2\text{H}_4 + \text{H}_2$	1.1 ± 0.4
$\rightarrow \text{SiH}^+ + \text{C}_2\text{H}_5$	0.73 ± 0.30
$\rightarrow \text{SiH}_2^+ + \text{C}_2\text{H}_4$	4.1 ± 1.6
$\rightarrow \text{SiH}_3^+ + \text{C}_2\text{H}_3$	10 ± 4
$\rightarrow \text{SiCH}_3^+ + \text{CH}_3$	0.32 ± 0.13
$\rightarrow \text{SiC}_2\text{H}^+ + 2\text{H}_2 + \text{H}$	0.10 ± 0.04

Reaction	$k \times 10^{10} (\text{cm}^3 \text{sec}^{-1})$
$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}_2 + \text{H}$	0.49 ± 0.20
$\rightarrow \text{SiC}_2\text{H}_4^+ + \text{H}_2$	0.18 ± 0.07
$\rightarrow \text{SiC}_2\text{H}_5^+ + \text{H}$	0.89 ± 0.36
$\text{Si}^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + \text{H}$	1.8 ± 0.7
$\text{SiH}^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + \text{H}_2$	1.5 ± 0.6
$\rightarrow \text{SiC}_2\text{H}_2^+ + \text{H}$	1.7 ± 0.7
$\text{SiH}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + \text{H}_2 + \text{H}$	0.44 ± 0.18
$\rightarrow \text{SiC}_2\text{H}_2^+ + \text{H}_2$	0.63 ± 0.26
$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}$	3.2 ± 1.3
$\text{SiH}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{SiC}_2\text{H}^+ + 2\text{H}_2$	0.1 ± 0.04
$\rightarrow \text{SiC}_2\text{H}_3^+ + \text{H}_2$	0.26 ± 0.10

With the exception of SiH_3^+ formation and reaction which we were not able to detect earlier,² the above results are in qualitative but not quantitative accord with the earlier study. This demonstrates once again^{4,5} the inadequacy of low-pressure, single-source techniques for the detailed study of ion-molecule reactions in systems containing more than one neutral reactant.

The high-pressure mass spectra show that the addition of small amounts of acetylene has a drastic effect on the ionic chemistry of monosilane with the principal reaction even in monosilane-rich mixtures being a termolecular association of SiH_3^+ with C_2H_2 , followed by further addition to this adduct of C_2H_2 molecules, i.e. an ionic polymerization

of C_2H_2 .⁶ In such monosilane-rich mixtures, all primary ions will tend to react with SiH_4 which, as shown by the table above and previous reports, yield SiH_3^+ on the predominant ion. At the higher pressures of the single-source study or in a radiolysis, SiH_3^+ reacts mainly by termolecular association.

It has been reported that in the γ -ray radiolysis of SiH_4 at 0.5 atm, the addition of acetylene results in an increase of $G(H_2)$ from 22.8 to 52.7.⁷ It seems apparent that this striking effect is associated with the drastic effect that we have found acetylene to have on the ionic chemistry of monosilane.

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5. ION-MOLECULE REACTIONS IN METHYLSILANE¹

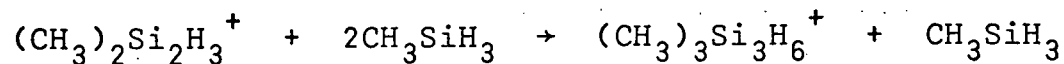
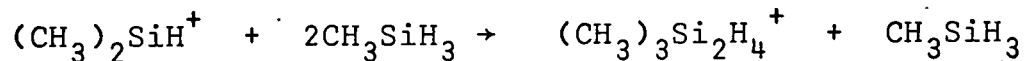
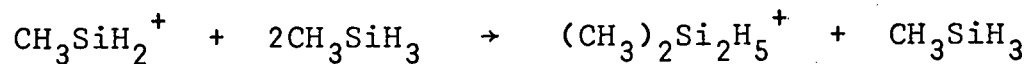
(COO-3416-15)

An earlier study of ion-molecule reactions in methylsilane was carried out in a single-source mass spectrometer and was limited to ion-source pressures below 0.006 torr.² In view of the possibility that these techniques and apparatus may have led to an incomplete characterization of this system, it was felt desirable to reinvestigate this system using the more refined techniques and apparatus now available in our laboratory.³ Accordingly, during the report year we have carried out tandem and high-pressure mass-spectrometric studies of this ion-molecule reactions occurring in pure methylsilane.

We have identified and measured phenomenological rate constants for twenty-six ion-molecule reactions involving the reactant ions: $\text{CH}_3\text{SiH}_2^+$, CH_3SiH^+ , CH_3Si^+ , CH_2Si^+ , CHSi^+ , SiH_3^+ , SiH_2^+ , SiH^+ , and Si^+ . Agreement of our results for the reactions of CH_3SiH^+ , which was the only reactant ion observed in the earlier study, is quite good, but the much more complete and extensive results of the present study obviously supercede those of the earlier one. As is characteristic of silane systems, the predominant mode of reaction is hydride-ion transfer from CH_3SiH_3 to the attacking ion, with isotope-labelling studies showing that the H^- transferred comes exclusively from those bound to silicon. A number of H-atom abstractions from CH_3SiH_3 also occur and it is shown that these transferred atoms also are originally bound to silicon. Thus it is concluded that the methyl group in CH_3SiH_3 plays no active role in the ionic chemistry of the molecule.

The high-pressure single-source studies are in complete accord with the bimolecular reactions identified by tandem mass spectrometry. In addition, the high-pressure studies reveal the

occurrence of the following termolecular association reactions:



Rate constants for these termolecular reactions as well as for the bimolecular reactions have been determined.

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6. KINEMATICS OF HYDRIDE-TRANSFER REACTIONS IN METHYLSILANE¹

(COO-3416-16)

The bimolecular ion-molecule reactions occurring in silanes and mixtures of silanes with other molecules are dominated by reactions whose net result is the transfer of the small particles, H^- , H_2^- , and H .²⁻⁵ However, at the beginning of the report year essentially nothing was known about the kinematics of such reactions. In this study we have carried out a kinematic analysis of these hydridic transfer reactions that are observed in ionized methylsilane using energy analysis of product ions and isotope labelling. The chemical reactions so studied along with their respective enthalpy changes were the following:

Reaction	ΔH° (kcal)
$CH_3SiH_2^+ + CH_3SiH_3 \rightarrow CH_3SiH_3 + CH_3SiH_2^+$	0
$CH_3SiH^+ + CH_3SiH_3 \rightarrow CH_3SiH_2 + CH_3SiH_2^+$	-1
$SiH_3^+ + CH_3SiH_3 \rightarrow SiH_4 + CH_3SiH_2^+$	-11
$SiH_2^+ + CH_3SiH_3 \rightarrow SiH_3 + CH_3SiH_2^+$	-11
$Si^+ + CH_3SiH_3 \rightarrow SiH_3 + CH_3Si^+$	+30
$Si^+ + CH_3SiH_3 \rightarrow SiH + CH_3SiH_2^+$	+10

It was found that all reactions proceed predominantly by a direct stripping-type process yielding product ions containing very little kinetic energy, which furthermore is independent of the reactant-ion kinetic energy, and also by an intermediate complex that is of greatest significance at low collision energies.

These results show that in methylsilane as in monosilane, the principal result of radiation-chemical significance of gas-phase ionization will be the formation of thermal energy ions of mass $(M-1)^+$ where M is the molecular weight of the molecules.

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7. ION-MOLECULE REACTIONS IN MONOSILANE-ETHYLENE MIXTURES¹

(COO-3416-17)

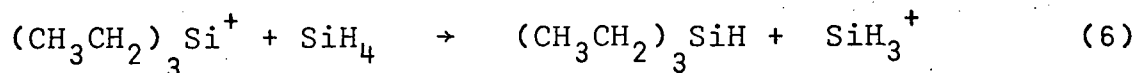
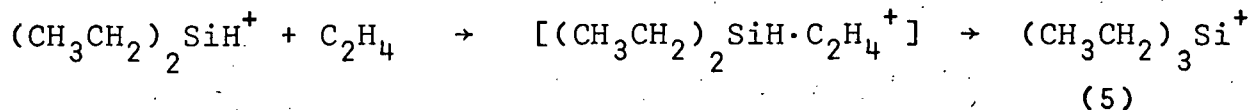
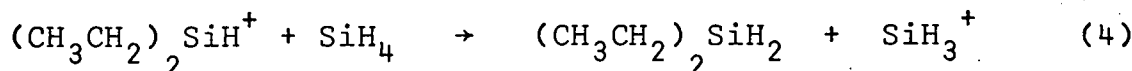
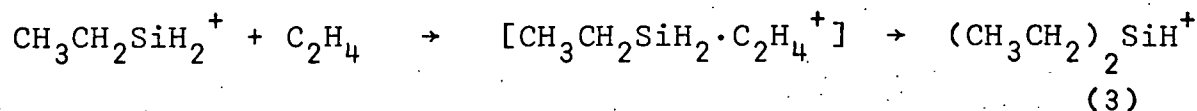
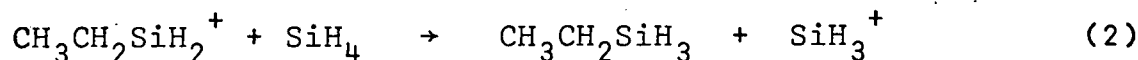
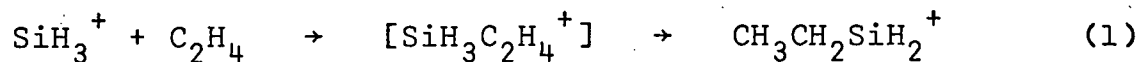
An earlier study of ion-molecule reactions in the $\text{SiH}_4\text{-C}_2\text{H}_4$ system was carried out at pressures below 0.005 torr in a single-source mass spectrometer, relying principally on appearance potential measurements of product ions for reaction identification.² More recent studies of ion-molecule reactions in similar systems^{3,4} using more sophisticated apparatus suggested that these early results may comprise a very incomplete picture of the ionic chemistry of the $\text{SiH}_4\text{-C}_2\text{H}_4$ system. Accordingly during the report year we have conducted further studies of this system using both tandem and high-pressure mass spectrometry.

As in the $\text{SiH}_4\text{-C}_2\text{H}_2$ system described earlier in this report only qualitative agreement with the earlier study² was obtained and we must conclude that single-source, low-pressure mass spectrometry is not adequate for the study of ion-molecule reactions in systems involving more than one neutral reactant. The present results thus supercede the earlier ones.

Twenty-six exothermic reactions involving reactions of SiH_3^+ , SiH_2^+ , SiH^+ , and Si^+ with C_2H_4 and C_2H_4^+ , C_2H_3^+ , and C_2H_2^+ with SiH_4 were identified and corresponding phenomenological rate constants measured. As in other silane systems studied, the principal reaction of pertinence to radiation chemical systems is hydride ion transfer from SiH_4 to the attacking ion.

A persistent, or "sticky", complex SiC_2H_7^+ is observed in collisions of low-energy SiH_3^+ ions with C_2H_4 ; the cross-section

for this process vanishes at a relative kinetic energy of 1.3 eV. Formation of this persistent complex in a bimolecular process is confirmed in the high-pressure single-source experiments. Further increases of pressure up to 0.3 torr show the successive addition of two more molecules of C_2H_4 with formation of the species $SiC_4H_{11}^+$ and $SiC_6H_{15}^+$, but the predominance of these adducts seems to be limited to three molecules of ethylene per SiH_3^+ . We believe that these adduct ions may be of central importance to the radiation chemistry of $SiH_4-C_2H_4$ mixtures in that they are precursors to the formation of ethylsilanes. A possible such reaction scheme is shown in (1)-(6). This chain process has also a free-radical



analog in which all siliconium ions are replaced by silyl radicals.

Previous studies of telomer formation in the radiolysis of $SiH_4-C_2H_4$ mixtures indicated that at least part of the $(C_2H_5)_2SiH_2$ telomer comes from non-radical reactions.⁵ The results of the

present study of ion-molecule reactions is of the utmost-importance to this radiation chemistry because we now know for the first time that SiH_3^+ ions will react rapidly with C_2H_4 .

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8. GAMMA-RAY RADIOLYSIS OF MONOSILANE-NITRIC OXIDE MIXTURES

At the beginning of the report year it was clear that the major products of the radiolysis of monosilane-nitric oxide mixtures were H_2 , N_2O , SiH_3OSiH_3 , Si_2H_6 , $SiH_3OSiH_2OSiH_3$, and $(SiH_3O)_3SiH$.

During the report year we have conducted γ -ray irradiations of a mixture containing 20% of nitric oxide. Analytical procedures to obtain quantitative radiolysis data are still being developed but the mass spectrometric procedures used to date yield the following approximate results for initial G-values.

<u>Reactant or Product</u>	<u>G($\frac{\text{molecule}}{100 \text{ eV}}$)</u>
SiH_4	-46
NO	-46
H_2	9.7
Si_2H_6	~ 0.6
SiH_3OSiH_3	~ 6
N_2O	?

The G-values for consumption of SiH_4 and NO indicate a chain reaction in which SiH_4 and NO participate on a 1:1 basis. The formation of Si_2H_6 in presence of NO when compared with the absence of such formation in the Hg-photo-sensitized SiH_4 -NO reaction¹ shows clearly that ionic processes must be involved² in the radiolytic formation of Si_2H_6 .

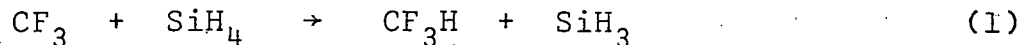
In the studies conducted we have had difficulties with the mass spectrometric determination of N_2O since there appears to be a low-level impurity in our initial mixtures that yields m/e 44.

References

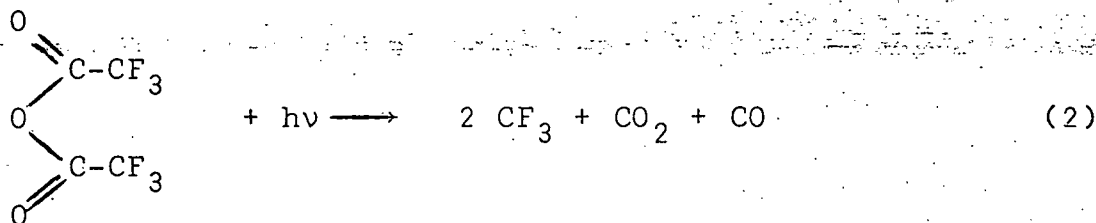
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9. PHOTSENSITIZED FORMATION OF SILYL RADICALS

At the beginning of the report year we had decided to use the well known reaction,¹ (1), as a source of SiH₃ radicals; the first

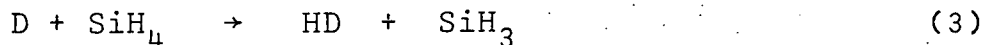


experiments showed conclusively that CF₃ radicals from the photolysis of CF₃N=NCF₃ did indeed produce SiH₃ under the conditions of our experiments. However, most of the CF₃ radicals react with the CF₃N=NCF₃ leading to a low yield of SiH₃ radicals. We then attempted to use as a source of CF₃ the photolysis shown by (2), since it had been reported² that CF₃ radicals do not react with this anhydride. The



formation of CF₃H showed that (2) was indeed followed by (1) as desired but that SiH₃ radicals were scavenged quickly by the anhydride, most probably through reaction with the carbonyl oxygen.³

We have now concluded that (1) should be abandoned as a source of SiH₃ radicals. Further we have found that the Hg-photosensitization of D₂-SiH₄ mixtures, containing a large excess of D₂, is an acceptable radical source⁴, via (3) since the D atoms react exclusively with



SiH₄ and SiH₃ radicals do not react at all efficiently with D₂.

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2. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Monosilane-Acetylene Mixtures". Submitted to J. Phys. Chem.
3. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Methylsilane". Submitted to J. Phys. Chem.
4. T. M. Mayer and F. W. Lampe, "Kinematics of Hydride-Ion Transfer Reactions in Methylsilane". Submitted to J. Phys. Chem.
5. T. M. Mayer and F. W. Lampe, "Ion-Molecule Reactions in Monosilane-Ethylene Mixtures". Submitted to J. Phys. Chem.

B. Lectures

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