MASTER

PROGRESS REPORT

August 31, 1978

REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

Department of Energy

Contract No. E(11-1)-1713

Period Covered: September 1, 1977 to August 31, 1978

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ABSTRACT

The experimental approach to attaining the goals of this research program is briefly outlined and the progress made in the last year is reviewed in sections entitled: a. Primary steps in the reaction of recoiling silicon and germanium atoms and the identification of reactive intermediates; b. Thermally induced silylene and germylene reactions; c. The role of ionic reactions in the chemistry of recoiling silicon atoms and other ion-molecule reactions studies; d. Silicon free radical chemistry.

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*This is DOE technical report No. COO-1713-76.

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Progress has been made in the last twelve months toward reaching the goals of this research program. These goals are: 1. Elucidation of the chemistry of recoiling silicon and germanium atoms and the manner in which their reactions take place, i.e., the operative reaction mechanisms; 2. Determination of the vibrational excitation and rates of rearrangement of reaction products; 3. Exploration of the reactions of atomic silicon and germanium with a variety of substrates; 4. To prepare by chemical means, and to study the reactions of, silicon and germanium radicals and ions which are probable reactive intermediates in recoil reaction systems.

To achieve these goals a wide range of experiments is carried out. High energy silicon and germanium atoms are created by nuclear recoil and their reaction products with various substrates are determined. The reaction substrates are chosen so that the products will elucidate the mechanisms of the recoil reactions. Information about the energy and electronic state of the recoiling atoms at reaction is obtained from the variation in product yields and the extent of decomposition and rearrangement of primary products as a function of total pressure and the concentration of inert moderator molecules that remove kinetic energy from the recoiling atoms. Recoil energy is conveniently varied by use of different nuclear reactions to generate the same species. The processes $^{31}\text{P}(n,p)^{31}\text{Si}$ and $^{76}\text{Ge}(n,2n)^{75}\text{Ge}$ both endow daughter nuclei with ca. 10^5 eV recoil energy, while $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ and $^{74}\text{Ge}(n,\gamma)^{75}\text{Ge}$ produce atoms with less than 10^3 eV recoil energy. The effect of energy and spin state on reactivity is also examined by studying the reactions of thermally evaporated silicon and germanium atoms with the same substrates with which the hot atoms are allowed to react.

Polyvalent recoiling atoms invariably initiate reaction sequences in which short-lived intermediate species are formed which react to form the

chemically stable end products that are actually detected.³³ Thus the hot atom chemistry of polyvalent atoms such as silicon and germanium encompasses the generation and study of interesting and highly reactive molecular and ionic species under mild conditions. The identification of the reactive intermediates has been an important facet of our research program. The reaction products from recoiling silicon and germanium atoms have been compared with products from specifically generated reactive intermediates such as SiH_n^+ ($n = 0, 1, 2, 3$), SiH_2 and SiH_3 . These comparisons have been helpful in confirming or eliminating the participation of these species in recoil reaction systems, and have been significant in themselves, providing new understanding of the little-understood chemistry of these reactive intermediates.

In studying the chemistry of SiH_5^+ it was found that the hydrogens are not chemically equivalent, and that the ion-molecule reactions, hydrogen ion transfer and molecular hydrogen elimination, could be used to study the structure of SiH_5^+ and CH_5^+ .^{34,35} This has led to an interest in employing ion-molecule reactions to study the structure of other gaseous ions.

The summary of research accomplishments during the past year is divided according to the above outline of our project into the following sections:

- a. Primary steps in the reactions of recoiling silicon and germanium atoms and the identification of reactive intermediates;
- b. Thermally induced silylene and germylene reactions;
- c. The role of ionic reactions in the chemistry of recoiling silicon atoms and other ion-molecule reaction studies;
- d. Silicon free radical chemistry.

Primary steps in the gas-phase reactions of recoiling silicon and germanium atoms and the identification of reactive intermediates.

It has recently become clear that silicon and germanium atoms recoiling from the $^{31}\text{P}(\text{n},\text{p})^{31}\text{Si}$ and $^{76}\text{Ge}(\text{n},2\text{n})^{75}\text{Ge}$ nuclear transformations behave quite differently from the thermally generated atoms.¹⁻³ The short-lived intermediates formed in the primary reactions of the recoiling silicon and germanium atoms also differ markedly from thermally generated species like SiH_2 , SiH_3 , GeH_2 and GeH_3 . Since the hot-atom reactions of silicon and germanium are not easily achieved by non-nuclear methods, these differences emphasize the importance of the recoil experiments in complementing thermal reaction studies and in extending the range of reactions beyond those accessible in thermal experiments.

An important continuing effort has been aimed at the identification of the important intermediates in the reactions of recoiling silicon and germanium atoms and the definition of the primary recoil reactions that give rise to them.

A useful mechanistic framework that has successfully related the structures of the major products to the substrate structures in the reactions of recoiling silicon atoms with a variety of silanes and other substrates has come under renewed scrutiny.^{2,3} We have postulated that recoiling silicon atoms acquire hydrogens, leading to the formation of silylene $^{31}\text{SiH}_2$, whose insertion (and addition) reactions lead to chemically stable products:^{4,5}

The hypothesis that silylenes are important intermediates in the reactions of recoiling silicon atoms has been an important heuristic tool, leading to the prediction of new reactions such as the addition of $^{31}\text{SiF}_2$ ⁶ and $^{31}\text{SiH}_2$ ⁷ to butadiene.

We have reported recently however that the relative reactivity of the intermediates in the reactions of recoiling silicon atoms toward silane and butadiene differs by a factor of ten from that of thermally generated silylene.³ Even more striking is the observation that the known silylene addition products⁸ are not observed in the reactions of recoiling silicon atoms with cyclopentadiene. Therefore if silylene $^{31}\text{SiH}_2$ is an important intermediate in these recoil systems, it must undergo reaction at high kinetic or vibrational energy or, as suggested by Tang,⁹ from an electronic state higher than the ground singlet state.

Mechanisms involving germylene intermediates $^{75}\text{GeH}_2$ have been proposed for the reactions of recoiling germanium atoms in germane-silane mixtures.¹⁰

Here too the formation of ground state germylene is brought into question¹ by the observation¹¹ that thermally generated GeH_2 does not insert into silicon-hydrogen bonds.¹²

In the past year experiments have been carried out to determine whether recoiling silicon and germanium atoms, when deprived of excess kinetic and electronic energy, will behave like thermally generated species and produce reactive intermediates that resemble ground state silylene and germylene in their reactions.

We have performed an extensive series of moderator experiments on the simplest recoil reaction system that gives high product yields - pure germane. In the absence of moderator the reactions of recoiling germanium atoms in pure germane give rise to three products: germane $^{75}\text{GeH}_4$, digermane $^{75}\text{GeGeH}_6$ and trigermane $^{75}\text{GeGe}_2\text{H}_8$ in combined yield of 35% at 2000 torr.¹⁰

Argon, Krypton and xenon moderators have been employed in two kinds of experiments. In a constant pressure series, as the moderator concentration increases, deactivation of vibrationally excited species by collisions with the gas molecules of the reaction mixture decreases in efficiency. Hence unimolecular decomposition of polyatomic intermediates and products increases together with the depletion of the kinetic and electronic energy of the recoiling atom. In a series of experiments at constant partial pressure of germane and varying moderator pressure, unimolecular decomposition decreases with degree of moderation.

In moderator experiments with varying total pressure there was a marked decrease in the yield of digermane and an increase in the trigermane yield. This interesting result suggests that a high energy germanium atom reacts with germane to ultimately form digermane product, while lower energy germanium atoms give trigermane as product. The alternative explanation that unimolecular decomposition is required for digermane formation is ruled out by the observation that an increase in pressure for pure germane reaction systems leads to an increase in the digermane and the trigermane yields. The effect of moderators and total pressure on product yields suggest that vibrationally or electronically excited polyatomic molecules as well as hot recoiling atoms participate in the reaction sequences. The similarity of the moderating efficiency of xenon and krypton may indicate that both the kinetic energy and electronic state of the recoiling germanium atom

are factors that determine the reaction channels that are followed.

While the intermediacy of germylgermylene $\text{H}^{75}\text{GeGeH}_3$ in the reactions of recoiling germanium atoms has been confirmed by these experiments, definition of the role of $^{75}\text{GeH}_2$ requires the detailed testing of contrasting mechanisms that fit the gross features of the moderator and pressure effect experiments. One mechanism currently being examined includes germylgermylene as the sole divalent intermediate:

An alternative mechanism involving two states of germylene is also being considered. Such a mechanism is in accord with the demonstrated difference between the behavior of the intermediates in the reactions of recoiling germanium atoms and that of thermally generated germylene:

Also in the past year experiments aimed at assessing the role of silylene $^{31}\text{SiH}_2$ in the reactions of recoiling silicon atoms have been carried out. The effects of moderator on the selectivity of the intermediates in the reactions of recoiling silicon atoms in mixtures of phosphine, silane and butadiene have been examined. Of particular interest is the ratio of disilane to sila-cyclopentene yields, since both products^{4,5,7} have been attributed to silylene intermediates via the partial mechanisms:

In the absence of moderator the product ratio is a linear function of the silane:butadiene substrate ratio, and the slope of the line indicated that

silane is ca. nine times as reactive as butadiene toward the reactive species for which these substrates compete.^{2,3} This is to be compared with the reactivity ratio of silane and butadiene toward thermally generated silylene, estimated to be 1.3 at 300° C. The product ratio in the recoil experiments has been found to decrease upon moderation, which is in accord with the intermediacy of excited silylene in unmoderated systems. Also in accord with the acquisition of monovalent atoms as a primary reaction of recoiling silicon atoms is the recent observation that $F_2^{31}Si$ and possibly $FH^{31}Si$ are apparent products when CF_4 is added to mixtures of phosphine and butadiene prior to fast-neutron irradiation. Silylenes have not been observed to abstract fluorine atoms from fluorocarbons¹³ (or hydrogen atoms from silanes³) so fluorine abstraction leading to $^{31}SiF_2$ formation, as suggested by Tang for PF_3 ⁶ is likely to precede addition to the diene. We have also recently detected fluorine atom abstraction in PH_3-CF_4 mixtures, leading to the formation of SiH_xF_{4-x} products.

Evidence has also been found in the past year, however, that can be construed as supporting a primary addition mechanism for reactions of recoiling silicon atoms with butadiene:

The formation of the cyclic silylene primary adduct has only recently been confirmed by the detection of products with empirical formula $^{31}SiC_8H_n$.

These and other newly detected products $^{31}\text{SiSiC}_4\text{H}_{10}$ (probably SiH_3SiH) and $^{31}\text{SiC}_4\text{H}_n$ will, it is hoped, assist in the unravelling of the primary reaction mechanisms for recoiling silicon atoms.

Experiments of this section were carried out by Bruce Cohen, Adam Helfer and Roger Woods.

Thermally induced silylene and germylene reactions

The reactions of probable intermediates in the chemistry of recoiling silicon and germanium atoms are being studied intensively in our laboratories. This is of great importance for the identification of product-forming intermediates in the recoil systems. As indicated in the section above on recoil experiments, it has been the increase in our knowledge of the reactivity of thermally generated silylene SiH_2 and germylene GeH_2 that has led to the recognition of important differences between the reactions of these species and those of the intermediates in the recoil systems.¹⁻³ To answer the question whether higher energy forms of silylene and germylene are important intermediates in the recoil systems we are continuing the study of thermally generated silylenes and germylenes both in order to better understand the reactions of these interesting species and to develop new chemical trapping reagents for them.

Having reported in the past year¹⁴ the first experiments on the gas-phase generation of dimethylgermylene Me_2Ge , we have begun to study its reactions. Three digermanes are employed as precursors that undergo unsymmetrical pyrolysis to the desired germylene

These are clean, high-yield, first-order reactions, and we employ them to generate dimethylgermylene in a low pressure fast-flow pyrolysis system in which residence time in the hot zone (450-600° C) is less than 0.1 sec. These conditions are relatively mild, since they have permitted the isolation of very labile products in analogous reactions of dimethylsilylene.^{8,15,16} The germylene precursors are also employed in sealed tube static pyrolysis experiments at 120-260° C.

We have found that dimethylgermylene is considerably less reactive than dimethylsilylene - while Ge-H, Ge-O and Ge-Cl bonds are all attacked by dimethylgermylene, products are formed in low yield. Other bonds, quite reactive toward dimethylsilylene, fail to react with dimethylgermylene. These include Si-H (see however footnote 12), C=C and C≡C. These latter bonds have all been reported as undergoing reaction with a variety of germynes in complex organometallic reactions whose mechanisms are poorly understood.¹⁷

Our results on dimethylgermylene agree with the only previous work in which an organogermylene GeEt_2 was definitely generated (but only in solution) and with the only reported studies of thermally generated gas-phase GeH_2 .^{19,20} It is likely that the bulk of the experiments in the literature which report the behavior of divalent germanium compounds are actually concerned with species other than free germynes, and that we are for the first time learning something about the chemistry of neutral compounds of divalent germanium.

In our studies of silylene reactions experiments have been undertaken on the generation of bis(trimethylsilyl)silylene $(\text{Me}_3\text{Si})_2\text{Si}:$. Three precursors $(\text{Me}_3\text{Si})_3\text{SiX}$ with $\text{X} = \text{H}, \text{Cl}, \text{OMe}$ have been synthesized as follows:²¹

All three compounds $(\text{Me}_3\text{Si})_3\text{SiX}$ undergo smooth unimolecular decomposition in solution:

Having previously shown that dimethylsilylene undergoes dimerization:¹⁵

it is anticipated that bis(trimethylsilyl)silylene will also dimerize, and in this case the steric bulk (and electronic influence) of the substituent trimethylsilyl groups may serve to stabilize the disilene. However, rearrangement of the original silylene prior to dimerization and of the disilene may also be anticipated:²²

In sealed tube static pyrolysis experiments preliminary results indicate that dimerization occurs but that the silicon-silicon double-bonded product undergoes oligomerization in preference to rearrangement.

In the past year we have pursued our studies of a highly intriguing silylene adduct tetramethylsilacyclopentene, obtained by the addition of dimethylsilylene to 2-butyne, and the first silacyclopentene ever obtained in stable form:¹⁶

While sensitive to air, moisture and metal surfaces, tetramethylsilacyclopentene is remarkably stable in solution when protected from the atmosphere.

In the past year we have demonstrated that photolysis with a medium pressure mercury lamp leads to quantitative extrusion of dimethylsilylene.

Addition reactions with various carbonyl compounds give stable cyclic products.

Not long ago this siloxacyclopentene ring system was regarded as highly unstable.²³ We have been able to grow large crystals of the fluorenone adduct for x-ray crystallographic determination of the exact geometry of the ring. These reactions provide additional chemical confirmation of the silacyclopentene structure, since similar adducts have been reported by Seyferth with substituted silacycloprenes.

An interesting new ring system is the apparent product of acetonitrile addition to tetramethylsilacyclopentene:

The experiments of this section have been carried out by Yue-Shen Chen, Becky Cornett and Eric Ma.

The role of ionic reactions in the chemistry of recoiling silicon ions

The low ionization potential of atomic silicon (8.1 eV) insures that if recoiling silicon atoms reached thermal energies as positive ions $^{31}\text{Si}^+$, ion-molecule reactions of high cross-section would be more efficient than neutralization.²⁵ Thus ion-molecule reactions could be important primary processes in the reactions of recoiling silicon atoms. We have found ion-molecule reactions with high cross-sections for thermal silicon ions Si^+ using ion cyclotron resonance spectroscopy,²⁶ and a feasible sequence of reactions leading from Si^+ to trisilane was observed.²⁵

The existence of reaction channels leading from silicon ions to neutral products observed in recoil experiments does not of course assure that

thermal silicon ions are important participants in the recoil reactions since the same products can arise from the reactions of neutral species.

We have carried out experiments employing tertiary amines Me_3N and Et_3N as ion scavengers since their ionization potentials are lower than that of silicon atoms. The results have been ambiguous because in the presence of carriers, product yields have decreased only at amine concentrations above 20%, even in the presence of a large excess of rare gas moderator. There is a definite effect, but it is small. There is however a large decrease in yield when trimethylphosphine replaces phosphine as the precursor for recoiling silicon atoms, even in the presence of an excess of silane, and this effect may be due to the low ionization potential of PMe_3 . Both the large decrease in product yields from recoiling silicon atoms due to trimethylphosphine and the smaller effect of trialkylamines affects all the major products. This is in accord with our finding^{2,3} that there is a common precursor for all the observed products.

Therefore in the past year, we have begun work once again on the reactions of gaseous silicon ions and their detection in recoil experiments. Ion cyclotron resonance experiments are being carried out on the reactions of Si^+ in $\text{PH}_3\text{-SiH}_4$ and $\text{PMe}_3\text{-SiH}_4$ mixtures. The goal is to simulate highly moderated recoil reaction mixtures to predict the full product spectrum to be expected from ion-molecule reactions of $^{31}\text{Si}^+$.

An interesting fragmentation process is also being studied. Electron impact on methylsilane MeSiH_3 produces Si^+ whose reactions with its precursor differ from reactions of Si^+ from SiH_4 . Specifically double resonance experiments indicate that the following reaction is exothermic for Si^+ from MeSiH_3 , but endothermic for Si^+ from SiH_4

This suggests that fragmentation of MeSiH_3 upon electron impact gives kinetically excited Si^+ ions, and this interpretation is supported by an observed decrease in efficiency in an exothermic ion-molecule reaction.

Experiments of this section were by James Dunbar with the assistance of Drs. Michael Sefcik and Jay Henis.

Silicon Free Radical Chemistry

Several years ago we found a new class of radicals from the addition of organosilyl radicals to the terminal nitrogen atom of diphenyldiazomethane:²⁷

R = Me

Et

ϕ

ϕ

R' = Me

Et

ϕ

H

At the same time a German group synthesized similar radicals containing no silicon atoms:²⁸

The silicon-substituted radicals have no spin-density in the pi-electron system and their esr spectra are characterized by the quite different nitrogen hyperfine coupling constants, and thus may be described as sigma-radicals. The radical from the phenylhydrazone of di-t-butyl ketone, on the other hand, has equal coupling constants for its two hydrogens, suggesting quite a different electronic structure. That this difference is related to the silyl substituent was demonstrated by the preparation of $(\text{t-Bu})_2\text{C}=\text{N}-\dot{\text{N}}\text{SiMe}_3$ whose esr spectrum closely resembles that of the other silyl-substituted iminanino radicals.

Therefore we have prepared a number of new iminamino radicals to study

the importance of steric and electronic factors in determining the structures of this new class of radicals as well as the specific effect of the silicon substituent. Berndt's group in Germany has shown that a sulfonyl substituent at the radical center has an effect similar to a silyl substituent and that open chain alkyl and aryl iminamino radicals all seem to be pi-radicals.²⁹

While Berndt has emphasized electronic effects in his discussion, we believe that nonbonding steric interactions can lead to twisting about the N-N bond imposing a rotational conformation that is a major determinant of the extent of spin delocalization.

We have found recently that the nitrogen hyperfine coupling constants for the following purely alkyl-substituted cyclic iminamino radical resembles those of acyclic alkyl iminamino radicals:

The nitrogen hyperfine coupling constants for the following acyclic iminamino radical with a strongly electron withdrawing, but first-row, substituent at the radical center are also equivalent indicating that electronegativity alone does not stabilize a sigma radical structure.

However a bulky and electronegative substituent does lead to a sigma-radical structure as indicated by the esr spectrum of the 2,3-dinitrophenyl-substituted radical:

We have synthesized the following radical precursors and are studying radicals derived from them:

In addition to these experiments we have examined the photolysis of *t*-butyl peroxide in low temperature (-78°) solutions containing silicon tetrafluoride. It was hoped that addition of *t*-butoxy radical would occur generating, for the first time, observable pentacovalent silicon radicals, previously postulated in the reaction of hydrogen atoms with silane.^{30,31}

In steady state photolysis the only radicals observed were from attack on the peroxide. Therefore if the pentavalent radical is formed it is short-lived and must be sought employing flash photolysis techniques.

These experiments were carried out by Roy Lewis.

In addition we have completed a collaborative study of the reactions of atomic chlorine with various gaseous hydrides at the Brookhaven National Laboratory. Chlorine atoms were produced by dissociation of Cl_2 by a microwave discharge in a fast gaseous flow system and atomic concentrations monitored by atomic resonance fluorescence spectroscopy using an apparatus designed and constructed by K. Y. Choo.³² Measured rate constants for reaction (by hydrogen abstraction) of chlorine atoms with SiH_4 , GeH_4 , PH_3 , AsH_3 and, for comparison, with CH_4 and C_2H_6 are shown in Table I. The rate

of reaction is seen to increase with decreasing Z-H bond strength for the reaction

The similarity of the reaction rates of silane and ethane suggests that chlorine atoms directly abstract hydrogen from silane rather than undergoing an addition-elimination process. These results have been submitted for publication.

These experiments were conducted by David Schlyer.

TABLE I

<u>Substrate</u>	<u>Bond Dissociation Energy (kcal/mole)</u>	<u>Rate Constant This Work (cc/molecule-sec)</u>	<u>Rate Constant Literature (cc/molecule-sec)</u>	<u>Substrate Concentration (molecules/cc)</u>	<u>Chlorine Atom Concentration (atoms/cc)</u>
CH ₄	104	$1.3 \pm 0.2 \times 10^{-13}$	$1.2 \pm 0.3 \times 10^{-13}$	$1.8 - 8.0 \times 10^{14}$	$1 - 10 \times 10^{12}$
C ₂ H ₆	98	$4.0 \pm 1.2 \times 10^{-11}$	$5.9 \pm 1.3 \times 10^{-11}$	$0.7 - 4.6 \times 10^{12}$	$2 - 10 \times 10^{11}$
SiH ₄	89-94	$3.6 \pm 2.0 \times 10^{-11}$	-	$0.7 - 4.7 \times 10^{12}$	$2 - 10 \times 10^{11}$
GeH ₄	87	$2.4 \pm 1.8 \times 10^{-10}$	-	$0.7 - 4.7 \times 10^{12}$	1×10^{11}
PH ₃	85-90	$6.0 \pm 1.8 \times 10^{-11}$	-	$0.5 - 2.7 \times 10^{12}$	$2 - 10 \times 10^{11}$
AsH ₃	58	$>2.0 \times 10^{-10}$	-	$<0.2 \times 10^{12}$	1×10^{11}
H ₂	104	-	$1.4 \pm 0.1 \times 10^{-14}$	-	-

PERSONNEL

In the past year several able coworkers have joined the research group and their efforts are just beginning to have an impact on the progress of this project.

Dr. Siu Hong Mo joined the group in August, 1978 having just completed a doctoral dissertation under the direction of Professor John Root at the University of California, Davis. His strong background in hot atom chemistry will allow rapid strides to be made in our studies of silicon and germanium recoil reactions.

Mr. James Dunbar, a first-year graduate student has begun work on the study of new silicon and carbon ion-molecule reactions and the role of ionic reactions in recoil systems. He already has several years of experience in the gas kinetics of silanes having worked as an undergraduate at the University of West Virginia with our former postdoctoral research associate, now Professor Gerald Stewart.

A new undergraduate research participant Roger Woods has begun studying silicon and germanium hot atom reactions, trained by graduating senior Bruce Cohen, who was awarded the Chemistry Department's highest honor the John Sowden prize as outstanding senior chemistry major as well as receiving his degree summa cum laude.

Second year graduate students Eric Ma and Yue-Shen Chen are making rapid progress. Mr. Ma is constructing an apparatus for thermal silicon and germanium atom reaction studies and is also investigating the reactions of dimethylgermylene and cyclic silylenes. Mr. Chen is studying the chemistry of bis(trimethylsilyl)silylene.

Advanced graduate students Becky Cornett and Roy Lewis are progressing rapidly toward their Ph.D. degrees. Ms. Cornett is studying dimethylsilylene

reactions and the chemistry of tetramethylsilacyclopentene. Mr. Lewis is involved with the effects of silicon both at and near a free radical center.

Adam Helfer, a junior, is beginning his second year in the group. He has completed the setting up of computer assisted data reduction for hot atom experiments, a task that required expertise in both hardware and software areas. In addition Mr. Helfer studies silicon hot-atom reactions.

Drs. Michael Sefcik and Jay Henis at Monsanto continue active collaboration on ion-molecule reaction studies and collaboration with Drs. David Schlyer and A. P. Wolf at the Brookhaven National Laboratory on atomic reaction studies in a discharge flow system are also continuing.

With five graduate students, two undergraduates and a postdoctoral fellow now working on this project, our strength has doubled in a year and we are now prepared to make rapid progress on all fronts.

STATEMENT OF EFFORT

During the preceding twelve months the principal investigator devoted approximately 25% of his time during the academic year to this project. He spent twelve weeks at Princeton University during the Fall of 1977 as Visiting Professor of Chemistry, but made three visits to St. Louis to confer with coworkers and spoke with coworkers by telephone twice a week. Seven weeks in the Summer of 1978 were spent in England. The rest of the summer was spent in the laboratory in St. Louis. The month of summer salary budgeted for this summer was in fact used to pay graduate student summer stipends.

PUBLICATIONS

In the past twelve months two papers were published:

1. COO-1713-52, M. Speranza, M.D. Sefcik, J.M.S. Henis and P.P. Gaspar, "Phenylum ($C_6H_5^+$) Ion-Molecule Reactions Studied by Ion Cyclotron Resonance Spectroscopy," J. Amer. Chem. Soc., 99, 5583 (1977).
2. COO-1713-56, K.Y. Choo and P.P. Gaspar, "An Absolute Rate Measurement by a Light Modulation ESR Technique," Journal of the Korean Chemical Society, 21, 270 (1977).

Three papers are in the press:

1. COO-1713-70, P.P. Gaspar and M.J. Welch, "Adendum to: 'Inorganic Hot Atom Chemistry in Gaseous and One-Component Liquid Systems,'" to be published with COO-1713-34 (same title), Nuclear Transformations in Solids, G. Harbottle and A.G. Maddock, Eds., North-Holland, Amsterdam, in the press.
2. COO-1713-71, P.P. Gaspar, "Recent Advances in Silylene Chemistry," Reactive Intermediates 1977, M. Jones, Jr. and R.A. Moss, eds. Wiley, N.Y., in the press.
3. COO-1713-73, R.-J. Hwang and P.P. Gaspar, "Reactions of Recoiling Silicon Atoms with Phosphine-Diene Mixtures and the Question of Silylene Intermediates," J. Amer. Chem. Soc., in the press.

One paper has been submitted for publication:

1. D.J. Schlyer, A.P. Wolf and P.P. Gaspar, "Rate Constants for the Reactions of Atomic Chlorine with Group IV and Group V. Hydrides," submitted to J. Phys. Chem.

In addition the principal investigator delivered an invited talk to the 12th. Organosilicon Award Symposium, Ames, Iowa on March 11, 1978, for which a manuscript was prepared: COO-1713-75, P.P. Gaspar, "Gas Phase Reactions of Silicon and Germanium Atoms."

References

1. P.P. Gaspar, "Gas Phase Reactions of Silicon and Germanium Atoms," an invited paper presented at the 12th Organosilicon Award Symposium, Ames, Iowa, March 11, 1978, COO-1713-75.
2. R.-J. Hwang, "The Role of Silylene (SiH_2) in the Chemistry of Recoiling Silicon Atoms," doctoral dissertation, Washington University, St. Louis, Dec., 1976, COO-1713-69.
3. R.-J. Hwang and P.P. Gaspar, "Reactions of Recoiling Silicon Atoms with Phosphine-Diene Mixtures and the Question of Silylene Intermediates," J. Amer. Chem. Soc., in the press, COO-1713-73.
4. P.P. Gaspar, P. Markusch, J.D. Holten, III and J.J. Frost, J. Phys. Chem., 76, 1352 (1972), COO-1713-24.
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9. O.F. Zeck, Y.-Y. Su, G.P. Gennaro and Y.-N. Tang, J. Amer. Chem. Soc., 96, 5967 (1974).
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11. M.D. Sefcik and M.A. Ring, J. Organometal Chem., 59, 167 (1973).
12. We have however observed $\text{Me}_3\text{SiGeH}_2\text{SiMe}_3$ as the only product from the cocondensation of thermally evaporated germanium atoms and trimethylsilane, and this result is most easily explained by postulating an Si-H insertion by a substituted germylene

The low yield (<5%) may speak for the inefficiency of the insertion or for the necessary participation of an excited state. See R.T. Conlin, S.H.

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