PROGRESS REPORT

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REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

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MASTER

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 in the recoil reactions; b. Thermally induced silylene and germylene reactions; c. Ion-molecule reaction studies.

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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 $^{31}\text{P}(\text{n},\text{p})^{31}\text{Si}$ and $^{76}\text{Ge}(\text{n},2\text{n})^{75}\text{Ge}$ both endow daughter nuclei with ca. 10^5 eV recoil energy, while $^{30}\text{Si}(\text{n},\gamma)^{31}\text{Si}$ and $^{74}\text{Ge}(\text{n},\gamma)^{75}\text{Ge}$ 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.¹ 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^+ .^{2,3} 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 in the recoil reactions;
- b. Thermally induced silylene and germylene reactions;
- c. Ion-molecule reaction studies.

PRIMARY STEPS IN THE GAS-PHASE REACTIONS OF RECOILING SILICON AND GERMANIUM ATOMS AND THE IDENTIFICATION OF REACTIVE INTERMEDIATES IN THE RECOIL REACTIONS

Recoiling silicon⁴⁻⁷ and germanium^{8,9} atoms produced in the $^{31}\text{P}(n,p)^{31}\text{Si}$ and $^{76}\text{Ge}(n,2n)^{75}\text{Ge}$ nuclear transformation undergo reactions quite different from their thermal counterparts.¹ The major products from reactions with silanes and germanes require the acquisition of hydrogen atoms by the recoiling metal atom, and this process does not occur with thermally evaporated silicon and germanium.^{10,11} In addition, products of consecutive insertion are also obtained in the recoil reactions.^{4-9,12,13}

Double insertions are known for chemically generated silicon and germanium atoms.^{10,11}

Much evidence has been obtained for the formation of divalent silicon and germanium radicals, silylene $^{31}\text{SiH}_2$ and germylene $^{75}\text{GeH}_2$, as the distinguishing feature of the recoil reactions. Both the insertion^{4,5} and addition^{14,15} reactions of SiH_2 inferred from recoil studies have been realized in thermal experiments.^{6,16,17}

A mechanism was thus suggested that accounts for the reactions of recoiling silicon and germanium atoms in terms of competing hydrogen acquisition and insertion by the recoiling atoms followed by insertion reactions of the divalent intermediate silylenes and germylenes:^{5,8}

It has also been recognized that ionic reactions could give some of the same products as the neutral pathway outlined above.¹⁸ Ionic condensation reactions have been observed both by Lampe,¹⁹ and by our laboratory.¹⁸

While the neutral pathway is believed to predominate, there are indications that ion-molecule reactions also contribute to product formation in the recoil systems.^{7,9} In addition, comparison of the relative reactivity of intermediates in the reactions of recoiling silicon atoms with that of thermally generated SiH_2 has revealed some interesting differences.⁷

We therefore suggested in our previous proposal a series of experiments devised to answer the following questions: 1. How does the reactivity of a recoiling silicon or germanium atom vary with energy? 2. Is the primary interaction of a recoiling silicon or germanium atom with a labile H-Z bond an insertion process or abstraction? 3. Is excited SiH_2 an important intermediate in the reactions of recoiling silicon atoms? 4. Are silicon and germanium ion-molecule reactions important in recoil systems?

Answers to these questions will permit the construction of an accurate and complete mechanism for a polyvalent recoiling atom for the first time. Silicon offers a favorable system for study since more than 70% of the recoiling atoms can be accounted for in simple volatile products.

Progress in the past year is reported in the following categories of experiments: a. Moderator and pressure effect studies of recoiling silicon atoms; b. Competition experiments with recoiling silicon atoms; c. Product studies and chemical trapping experiments; d. Experiments to test the role of ion-molecule reactions in silicon recoil systems; e. Germanium atom recoil experiments.

a. Moderator and pressure effect studies of recoiling silicon atoms

Previous experiments with rare gas moderators indicated that the major product from reactions of recoiling silicon atoms in phosphine silane mixtures, disilane $^{31}\text{SiH}_3\text{SiH}_3$ (formed in 48% absolute yield in 1:1 mixtures at 1000 torr) has a kinetically excited precursor.^{4,7}

In the past year a polyatomic moderator molecule, ethane, was chosen to investigate the role of vibrational excitation in intermediates and products. It was found that with increasing ethane pressure (and constant $\text{PH}_3\text{-SiH}_4$ partial pressure) the disilane yield does decrease but the moderator effect is smaller than that observed with other noble gases.

Since ethane should efficiently deactivate hot silicon atoms from transfer of kinetic energy, as well as cooling vibrationally excited molecular intermediates and products, the most likely explanation for the small decrease in disilane yield in the presence of ethane is that ethane itself can react with high energy silicon atoms in a process that ultimately forms disilane.

The alternative explanation that ethane depresses the disilane yield by suppressing unimolecular decomposition

is rendered unlikely by pressure effect studies in which the yields of all the major products, silane, disilane, and trisilane, stayed constant with increasing total pressures of 1:1 $\text{PH}_3\text{-SiH}_4$ mixtures over the same pressure range as the ethane moderator experiments.

If high-energy reactions of ethane with recoiling silicon atoms compete with moderating collisions, hydrogen abstraction, rather than insertion, is indicated as the bond forming process, since no ethylsilane products are observed.

Another interesting facet of the ethane experiments is the decrease in silane yield with increasing ethane pressure. Since this is not due to a collisional deactivation of vibrationally excited disilane, either moderating or reactive collisions with ethane must compete with reactions that produce silane. One possibility is a high-energy redistribution reaction, a fragmentation of a collision complex, e.g.:

A moderator experiment with krypton was carried out to 93% mole fraction moderator in order to search for a limiting yield plateau indicative of multiple reaction pathways leading to the formation of disilane. No such plateau was found, the yield of disilane, 42% in the absence of moderator, 11% at 93% moderator, clearly tending to zero. Thus there seems to be only a high energy path to the disilane product.

An interesting feature of the moderator experiments, both with noble gases and ethane is the constancy of the trisilane yield. A decrease in the disilane yield does not lead to an increase in the yield of trisilane, which is nearly invariant to moderator concentration. This suggests a path for trisilane formation quite independent from that for production of disilane. Differences in charge state or electronic state are indicated.

b. Competition experiments

In the past year we have continued to examine the relative reactivity of methylsilane and silane toward the intermediates in the reactions of recoiling silicon atoms with phosphine-silane mixtures. This pair of substrates was chosen because of the careful measurement of their relative reactivity toward thermally generated ground-state singlet silylene by Paquin and Ring.²⁰

$$E_a^{(1)} - E_a^{(2)} = 4.2 \pm 1.2 \text{ kcal/mole}$$

$$\log (A_1/A_2) = 1.7 \pm 0.4$$

The relative reactivity was measured by Paquin and Ring in the temperature range 246 to 287° C. The availability of the relative activation parameters permitted an extrapolation to room temperature and a prediction that completely relaxed ³¹SiH₂ in a recoil system would react an order-of-magnitude more rapidly with silane than with methylsilane.

We reported a year ago that in an unmoderated recoil system, methylsilane is 1.34 ± 0.02 as reactive toward SiH₃CH₃ as toward SiH₄.⁷ We have now found that this reactivity ratio is only slightly altered by 90% moderator, nitric oxide free radical scavenger, and a combination of both. This seems to rule

out excess kinetic energy and an excited triplet $^{31}\text{SiH}_2$ as the source of the anomalous reactivity.

Excess vibrational energy, a "hot" silylene was also eliminated as the cause of reduced selectivity by use of ethane quencher. We next turned to recoil experiments at elevated temperatures. We found little difference between the selectivity at 200° C and 25° C.

Thus if one accepts the activation parameters of Paquin and Ring,²⁰ then there are distinct reactivity differences between the intermediates formed from recoiling silicon atoms and thermally generated SiH_2 . However it should be noted that the relative reactivity observed in the recoil system 1.1 to 1.3 is very similar to that found by Paquin and Ring, 0.97 to 1.3. Therefore if the difference between the activation parameters for insertion into methylsilane and silane are really much smaller than reported, the recoil experiments would be in accord with a silylene intermediate.

It is interesting that the relative reactivity of silane and butadiene toward recoiling silicon atoms does respond to moderation, and in just the way expected for $^{31}\text{SiH}_2$.

c. Product studies and chemical trapping experiments

One of the problems in distinguishing ionic from neutral recoil reactions via product studies is the general similarity of the reactions of electron deficient silicon species - neutral and ionic. Therefore we have sought reactions specific either to neutral or ionic silicon radicals. One discussed more fully below is the silylene-to-silylene rearrangement, first reported by Barton,²¹ and also investigated in our laboratory.²²

If neutral silicon atoms insert into Si-H bonds of trimethylsilane, the following sequence is predicted:

This rearrangement has been realized in the thermal generation of the silicon atom insertion product; in overall yield 45%.²³

Evidence has been found that the rearrangement also occurs in the recoil system.²³ In fact the final product 1-methyl-1,3-disilacyclobutane is not obtained in the recoil reaction, but a product is found from interception of an intermediate in the rearrangement:

The same product is obtained in low yield when $\text{Me}_3\text{Si}-\ddot{\text{Si}}\text{H}$ is generated thermally in the presence of excess trimethylsilane.²³

Thus this result confirms that insertion by neutral silicon atoms does occur in recoil reactions.

d. Experiments to test the role of ion-molecule reactions in silicon recoil systems

We reported a year ago the identification of 1,1,1,2-tetramethyldisilane as the product formed in second highest yield from the reactions of recoiling

silicon atoms with trimethylsilane.⁷

Since alkyl group abstraction has been found in ion-molecule reactions of carbon and silicon cations with alkylsilanes,²⁴⁻²⁶ the formation of 1,1,1,2-tetramethyldisilane has been taken as evidence for the participation of ion-molecule reactions in silicon recoil systems.

In the past year we have found an analogous methyl transfer in the reactions of recoiling silicon atoms with methylsilane.

It is also clear that there are redistribution reactions of neutral insertion products that could account for methyl transfer:

An experiment has been initiated that promises to assess the relative contributions of neutral and ionic processes in silicon recoil reactions. We have pointed out that t-butylethylene can be expected to yield products containing t-butyl groups from addition of neutral silicon radicals, but rearranged products from ion-molecule reactions.

We have found that $\text{H}_3^{31}\text{Si}-\text{CH}_2-\text{C}(\text{CH}_3)_2$ is formed albeit in only 1% yield in recoil reactions. Another product produced in similar yield is not the other unrearranged $\text{H}_3^{31}\text{Si}-\text{CH}=\text{C}(\text{CH}_3)_2$. Authentic rearrangement products are being synthesized to facilitate its identification.

e. Germanium atom recoil experiments

Our model for the reactions of recoiling germanium atoms in germane is being developed to accomodate the following observations:

- i. The yield of degermane is reduced by both noble gas moderators and by ethane. Ethane is least effective and krypton most effective.
- ii. The yield of trigermane is insensitve to moderator.
- iii. Silane does not act as a moderator for recoiling germanium atoms in germane-silane mixtures.
- iv. Methylgermane is among the products from reactions of recoiling germanium atoms in trimethylgermane.

The present model includes both ionic and neutral processes, and can be summarized as follows:

In the past year we have found some contributions from reactions of ^{77}Ge (and ^{75}Ge) formed in high-energy (n,γ) reactions. Use of monochromatic 14 MeV

neutrons eliminates these (n,γ) processes.

The experiments of this section have been carried out by Dr. Siu-Hong Mo, Adam Helfer, and Roger Woods.

THERMALLY INDUCED SILYLENE AND GERMYLENE REACTIONS

The study of thermally generated divalent silicon and germanium radicals in parallel with recoil studies has provided important comparisons for the interpretation of recoil reactions, but the new reactions of silylenes and germylenes hold great interest in themselves.

We have completed our characterization of tetramethylsilacyclopentene,²⁷ a new class of compounds first produced in our laboratory by a silylene addition reaction²⁸

We have found that Lewis base catalyzed oligomerization of the silylcyclopropene leads to dimer as well as polymer formation.²⁷ Such a process explains the thermal "dimerization" of silacycloprenes in solution, but not in the gas phase.²⁹

Two spectacular discoveries have been made in the study of the thermal and photochemical decomposition of methoxytris(trimethylsilyl)silane.

Solution thermolysis in the absence of added trapping reagents has yielded the cyclic tetramer of the silylene.³⁰

Photolysis of $(\text{Me}_3\text{Si})_3\text{SiOMe}$ has been found to yield two different silylenes in high yield.³⁰ This is by far the most efficient photochemical route to silylenes. The silylenes have been trapped with both butadienes and acetylenes.

These results indicate that in contrast to the thermal decomposition of $(\text{Me}_3\text{Si})_3\text{SiOMe}$ in which methoxy migration (process b below) predominates, trimethylsilyl group migration (process a) also occurs in essentially the statistical ratio $a:b = 2:1$. This was confirmed in the observation of the statistical ratio of processes $c:d = 1:2$ in the photolysis of $(\text{Me}_3\text{Si})_2\text{Si}(\text{OMe})_2$

We have found that the methoxy group strongly activates a polysilane toward photolysis, and thus methoxy polysilanes are valuable precursors for photochemical generation of silylenes.

The silylene $\text{MeO}-\ddot{\text{Si}}-\text{SiMe}_3$ that we have made for the first time is of some importance in carrying groups that can both be removed, thermally or photochemically, from a silylene adduct, regenerating a silylene. This silylene is therefore a potential silicon atom synthon, a synthetic equivalent of a silicon atom, and we have demonstrated this in the laboratory. Photochemical generation of $\text{MeO}-\ddot{\text{Si}}-\text{SiMe}_3$ and addition to butadiene, followed by pyrolysis of the adduct in the presence of excess butadiene led to the formation of the spirosilanona-diene found last year in a recoil reaction.³³

We have also employed the thermal generation of bis(trimethylsilylsilylene) to demonstrate that addition of a silylene to an acetylene can occur at high temperature in solution. The silacyclopentene adduct was indicated by its rearrangement product.

The occurrence of this thermal addition is of course well documented in the gas-phase and led us to the first isolable silacyclopentene²⁸, but in solution this reaction has been controversial.^{29,34}

In the past year our study of thermally generated dimethylgermylene has progressed.³⁵ Both pentamethyldigermene and chloropentamethyldigermene are clean sources of dimethylgermylene in solution, as has been demonstrated by kinetic studies. The divalent germanium radical has been trapped by insertion into Ge-H and Ge-Cl bonds.

The chloropentamethyldigermene is also clearly decomposed to dimethylgermylene in the gas-phase, and is making possible for the first-time study of the gas-phase chemistry of an organogermylene. In preparation for gas-phase trapping experiments, authentic adducts have been synthesized, e.g.³⁶

The experiments of this section have been carried out by Dr. Becky Cornett (tetramethylsilacyclopentene), Yue-Shen Chen (silylenes from methoxytris(trimethylsilyl)silane), Eric Ma (dimethylgermylene) and Ken Kobayashi (synthesis of germylene adducts).

ION-MOLECULE REACTION STUDIES

In the past year we have begun our study of the reactions of phenyl cations C_6H_5^+ by ion cyclotron resonance spectroscopy. The singlet state of this ion is of interest to us because its electronic structure resembles that of a doubly excited carbene, silylene or germylene.

We therefore hope that the behavior of the phenyl cation will tell us something about the reactions of electronically excited silicon and germanium species which we are studying by recoil and chemical methods.

We have found the following reactions in the past year:

This reaction is best formulated as an attack on the oxygen atom followed by cleavage of a methyl radical. This seems to be a reaction of an empty sigma-orbital accepting an oxygen lone pair of electrons.

While the latter process can be formulated as attack at the oxygen similar to that written above, the first two seem to be reactions involving C-H, C-O, or even C-C bonds and may be due to a radical-like reaction.

Here again the processes leading to $C_6H_6O^+$ and $C_6H_7O^+$ can be formulated as reactions of an empty sigma-orbital on $C_6H_5^+$ with the oxygen of the alcohol acting as a Lewis base. The formation of $C_7H_7^+$ could be regarded as a C-H insertion followed by loss of water.

We have begun a search for reaction substrates whose ion-molecule reaction products will not only illuminate the chemistry of the phenyl cation, but reveal its electronic structure at reaction.

The reaction of phenyl cation with ethane that leads to H_2 transfer

has been studied with isotopically labelled ethane CH_3CD_3 . It has been found that HD transfer is the dominant, but not exclusive process.³⁷

The experiments of this section were carried out by Mr. James Dunbar.

PERSONNEL

Dr. Siu Hong Mo spent a second fruitful year working on the reactions of recoiling silicon atoms, and will move to a position in nuclear pharmaceutical chemistry and nuclear medicine. He will be succeeded on September 1, 1980 by Dr. Stanislaw Konieczny from the Technical University, Gdansk, Poland. Dr. Konieczny has worked with Professor Wojnowski on the mechanisms of organo-silicon reactions. In St. Louis he will work on the reactions of thermally evaporated silicon and germanium atoms and on new routes to silylenes and germylenes.

In May 1980 Dr. Becky Cornett received her Ph.D., with a dissertation describing the characterization and reactions of tetramethylsilacyclopropene.

Fourth year graduate students Eric Ma and Yue-Shen Chen have made considerable progress in the study of organogermynes and silylenes and have both had papers accepted for publication in the past year. Their work provided the basis for the Principal Investigator's invited lecture at the XIV Organosilicon Symposium held at Texas Christian University March 28,29, 1980. Third year graduate student James Dunbar has discovered interesting new reactions of phenyl cations in the gas phase, employing ion-cyclotron resonance spectroscopy.

The undergraduate members of the research group are doing outstanding work, as usual. Adam Helfer found the long sought spiro-adduct of recoiling silicon atoms and butadiene before graduating in January, 1980. He was honored by being awarded a Rhodes Scholarship for study in mathematical physics at Oxford. He is the second Rhodes Scholar from this group; the first was Steven Lockhart in 1977. Roger Woods, who completely rethought our model for the reactions of recoiling germanium atoms, graduated in June 1980, having been awarded the John Sowden Memorial Prize as the outstanding graduating chemistry major in 1980. Roger will begin medical studies at the Harvard University School of Medicine in the fall. With two outstanding undergraduates leaving it is pleasant to report that three exceptionally able undergraduates have joined the group. Eric Suchanek is continuing work on recoiling germanium atoms and also ministering to our computer. Ken Kobayashi is studying chemically generated halogermynes. Peter Bushonow will work on the reactions of recoiling silicon atoms.

In August 1980 one postdoctoral fellow, three graduate students and three undergraduates are at work on this project.

STATEMENT OF EFFORT

During the preceding twelve months the Principal Investigator devoted approximately 25% of his time during the academic year to this project. Six weeks in May and June of 1980 were spent in England. The rest of the summer was spent in the laboratory in St. Louis,

PUBLICATIONS

In the past twelve months two papers were published:

1. COO-1713-82, Becky J. Cornett, Kwang Yul Choo and Peter P. Gaspar, "Disproportionation of Trimethylsilyl Radicals to a Silaolefin in the Liquid Phase," J. Am. Chem. Soc., 102, 377 (1980).
2. COO-1713-87, Eric C.-L. Ma, Don P. Paquin, and Peter P. Gaspar, "Thermal Generation of Dimethylgermylene and its Insertional into the Germanium-Hydrogen Bond," J. Chem. Soc. Chem. Comm., 381 (1980).

Three papers are in the press:

1. COO-1713-81, Peter P. Gaspar and John W. Root, "Kinetics, Mechanism and Hot Atom Chemistry - Present Perspectives and Future Goals," Radiochimica Acta, in the press.
2. COO-1713-86, Yue-shen Chen, Bruce H. Cohen and Peter P. Gaspar, "Rearrangement of Bis(trimethylsilyl)silylene (Me_3Si)₂Si in the Gas Phase," J. Organometal. Chem., in the press.
3. COO-1713-88, Peter P. Gaspar, "Advances in Silylene Chemistry 1977 to 1979," Reactive Intermediates, Vol. 2, M. Jones, Jr. and R.A. Moss, eds. Wiley, N.Y., in the press.

One paper has been submitted for Publication:

1. COO-1713-92, Peter P. Gaspar, "Recoil Chemistry and Mechanistic Studies with Polyvalent Atoms," ACS symposium volume Recent Developments in Biological and Chemical Research with Short-Lived Isotopes, K. Krohn and J.W. Root, eds. submitted for publication.

In addition the dissertation of Dr. Becky Cornett was completed: COO-1713-90, Becky June Cornett, "Tetramethyl-1-silacycloprop-2-ene; its Characterization and Reactions," doctoral dissertation, Washington University, May, 1980.

In January 1980 the Principal Investigator was invited to deliver a plenary lecture on higher group IV carbene analogs to the Ninth Okazaki Conference, "The Molecular Design of Reactive Intermediates - the Case of Carbenes" held at the Institute for Molecular Science, Okazaki. During the period I was in Japan, from January 6 to January 27, I was also invited to give lectures at the Universities of Kyoto, Sendai, Tsukuba and Tokyo. The lecture at Okazaki will be published as technical report COO-1713-91.

In March, 1980 the Principal Investigator was invited to present a lecture, COO-1713-89, "Recent Developments in the Chemistry of Silylenes and Germylenes" at the XIV Organosilicon Symposium at Texas Christian University, Fort Worth to honor Professor Evelyn Ebsworth on his receipt of the Kipping Award in Organosilicon Chemistry presented by the American Chemical Society.

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