PROGRESS REPORT

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REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

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ABSTRACT

In the last year progress has been made in the following major areas:

- a. Primary steps in the reactions of recoiling silicon and germanium atoms;
- b. The role of ionic reactions in the chemistry of recoiling silicon atoms;
- c. Other ion-molecule reaction studies;
- d. Silylene reaction studies;
- e. Thermal evaporation of germanium atoms;
- f. Study of silyl radicals by electron spin resonance spectroscopy;
- g. Study of abstraction of moieties other than hydrogen by recoiling silicon atoms.

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Considerable 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.

This summary of research accomplishments during the past year is divided into the following sections: a. Primary steps in the reactions of recoiling silicon and germanium atoms; b. The role of ionic reactions in the chemistry of recoiling silicon atoms; c. Other ion-molecule reaction studies; d. Silylene reaction studies; e. Thermal evaporation of germanium atoms; f. Study of silyl radicals by electron spin resonance spectroscopy; g. Study of abstraction of moieties other than hydrogen by recoiling silicon atoms.

Primary steps in the reactions of recoiling silicon and germanium atoms.

In the past year the use of butadiene as a mechanistic probe in the reactions of recoiling silicon and germanium atoms has proved quite fruitful and has led to new directions in our thinking.

It has been found that addition of butadiene to phosphine-silane mixtures prior to neutron irradiation leads to a reduction in yield of all three major products of the reactions of recoiling silicon atoms - silane, disilane and trisilane. The decrease in yield expressed as a

fraction of the yield in the absence of butadiene is the same for all three of these products.

This suggests that a common precursor of the three products is being scavenged by the butadiene and that trisilane, like silane and disilane, is formed from neutral reaction intermediates.

A surprising result was the finding of only a small amount of sila-cyclopentene as product from 1:1 phosphine-silane recoil reaction mixtures containing sufficient butadiene (10%) to depress the yields of silane, disilane and trisilane by 50% relative to yields obtained in the absence of butadiene.

Based on previous models for the phosphine-silane¹ and phosphine-butadiene²⁻⁴ recoil reaction systems the following reactions were anticipated for the phosphine-silane-butadiene system:

(products detected are underlined)

Since we have found that ground state singlet silylene reacts with butadiene ca. ten times as rapidly as with disilane, a high yield of silacyclopentene $^{31}\text{SiC}_4\text{H}_8$ should have been obtained from a 1:1 PH_3 , SiH_4 mixture containing 10% butadiene, if $^{31}\text{SiH}_2$ (as a thermal ground state singlet species) is the precursor for the disilane product formed in nearly 30% absolute yield.

Thus we infer that the dominant reactive intermediate formed by recoiling silicon atoms in phosphine-silane mixtures is not thermal ground state silylene.

When silane is added to phosphine-butadiene mixtures a decrease is observed in the yields of the two products formed in the absence of silane, $^{31}\text{SiC}_4\text{H}_8$ silacyclopentene and $^{31}\text{SiC}_4\text{H}_6$ believed to be silacyclopentadiene. Again the decreases in yield are identical, relative to yields obtained without silane. This suggests once again the trapping of one or more common intermediates. Since the presence of silane should cause an increase in the amount of radioactive silylene formed, and since butadiene is more reactive than silane toward thermal ground state singlet silylene, the decrease in the yield of silacyclopentene upon the addition of a small amount of silane suggests the importance of other intermediates.

That the formation of ground state singlet thermal silylene is unimportant in phosphine-silane recoil reaction systems is also indicated by experiments in which cyclopentadiene was present in the reaction mixtures. Again the yields of silane, disilane and trisilane decreased without the formation of the singlet silylene adduct 1-sila-2,4-cyclohexadiene.⁵

While the recoil reaction systems may produce $^{31}\text{SiH}_2$ in kinetically excited form or in spin states (e.g. triplets) other than the ground state singlet, silylene may be only a minor intermediate in the recoil systems.

Alternative reaction sequences may be envisioned, such as the following model for the phosphine-silane and phosphine-butadiene systems:

Thus in the past year experiments which were designed to determine whether nucleogenic disilane and trisilane are both formed from neutral intermediates and also whether silacyclopentene and silacyclopentadiene have the same precursor have led to the reexamination of the role of silylene ${}^{31}\text{SiH}_2$ in recoil systems and to a search for other important intermediates.

The reactions of recoiling germanium atoms have also received renewed attention in the past year. In previously published studies^{6,7} the following reaction scheme was proposed for germanium atoms recoiling in pure germane:

The products detected are underlined in the above reaction scheme.

This reaction sequence is similar to the scheme previously proposed for recoiling silicon atoms in phosphine-silane mixtures and which is currently being reexamined. Therefore we have employed ethylene and butadiene as substrates for reactive intermediates to determine whether the products observed from pure germane are derived from different reactive intermediates as proposed in the above scheme. We have found recently that the yields of all three products $^{75}\text{GeH}_4$, $^{75}\text{GeGeH}_6$ and $^{75}\text{GeGe}_2\text{H}_8$ decrease with increasing amounts of ethylene and butadiene. Preliminary results indicate that all three yields decrease equally relative to yields in pure germane. Furthermore ethylene is less effective than butadiene at decreasing the product yields.

While it is possible that the relative reactivity of olefins and germane toward GeH_2 and GeH_3GeH are the same, thus reconciling the observed results to the proposed reaction sequence, it is unlikely. Therefore the new evidence suggests a common precursor for the three products, possibly $\text{H}-^{75}\text{Ge}-\text{GeH}_3$, which may be capable of abstracting hydrogens as well as inserting into Ge-H bonds.

The work of Mr. Hwang, Mr. Cohen and Mr. Lockhart has provided new insight into the primary reactions of recoiling silicon and germanium atoms by forcing us to reexamine the models we previously proposed. While the previous models have been successful in explaining both our results and those of other workers, there seems little question that the present experiments will lead to considerable refinement of these models in the immediate future.

The role of ionic reactions in the chemistry of recoiling silicon atoms.

In the past year the yield of trisilane from the reactions of recoiling silicon atoms in phosphine-silane mixtures has been carefully determined as a function of the amount of amine scavenger present, using small amounts of trisilane as internal carrier. This experiment has been an important step in our effort to determine whether silicon ions $^{31}\text{Si}^+$ play an important role in the chemistry of recoiling silicon atoms. We have previously demonstrated that a reaction sequence initiated by Si^+ can give rise to trisilane under the recoil reaction conditions^{2,3,8} and that Si^+ reacts rapidly with simple amines.^{3,8}

Without internal trisilane carrier, the trisilane yield had previously been found to decrease with increasing amine concentrations,³ a result compatible with the incursion of ionic processes, but the results were somewhat erratic. In the presence of trisilane internal carrier the yield of radioactive trisilane does not decrease appreciably in the presence of as much as 25% amines.

While this result calls into question the previous evidence for the intervention of $^{31}\text{Si}^+$ in the reaction sequence leading to radioactive trisilane,^{2,3,8} an important role for ionic reactions in silicon atom recoil chemistry has not been definitively excluded. The observation that phosphine, present in much larger concentration than amines in recoiling reaction systems, also reacts efficiently with Si^+ ions suggests that any recoiling silicon ions $^{31}\text{Si}^+$ may react with phosphine. Thus the large amounts of PH_3 present may mask the effects of added substrates capable of capturing silicon ions.

The reactions of silicon ions with benzene were investigated by ion cyclotron resonance spectroscopy of silane, benzene mixtures. Si^+ was

found to react with benzene in the following reaction:

Other reactions observed include:

The latter reactions are fascinating in that the ionic product has the stoichiometry of a silatriopylium ion. Its structure is being investigated.

Having demonstrated that Si^+ react efficiently with benzene, we have begun to study the reactions of recoiling silicon atoms with benzene. Phosphine-benzene and phosphine-silane-benzene mixtures do not yield phenylsilanes as reaction products, only polymeric material being obtained.

The experiments of this section were carried out by Dr. Speranza and Mr. Mizes, with continuing advice and assistance from Dr. Sefcik.

Other ion-molecule reaction studies.

During the past year Maurizio Speranza, from the Laboratorio di Chimica Nucleare Del Consiglio Nazionale delle Ricerche, Rome, has been in Saint Louis applying ion cyclotron resonance spectroscopy to the elucidation of the mechanism of the gamma radiolysis induced protodehalogenation reaction.⁹ In this process strong proton donors H_3^+ or CH_5^+ are produced which then react with halobenzenes to replace the halogen atom with a hydrogen, e.g.:

Ion cyclotron resonance spectroscopic studies have now clearly demonstrated that the following mechanism operates:^{9c}

In addition to a rapid protodehalogenation reaction via what appears to be a stripping process, protodehalogenation can occur with isotopic exchange:

Simple protonation can also take place:

The extent to which the various reactions of the proton donor with the halobenzene occur varies with the nature of the protonating agent and the halogen atom present. CH_2^+ , CH_3^+ , CH_4^+ , CH_5^+ , and H_3^+ have been studied as the Brønsted acid and ϕF , ϕCl and ϕBr were the halobenzenes studied.

The unique capability of the double resonance technique in ion cyclotron resonance spectroscopy to connect reactant and product ions in ion-molecule reactions has been found to complement the end product studies carried out by Cacace and coworkers using tritium labelling methods.⁹ The icr experiments have provided direct information about ionic reaction sequences which, when combined with the labelling studies, have clarified the high pressure radiation experiments.⁹

The convenience of protodehalogenation as a means for the production of phenyl cations has been exploited for the study of phenyl cation reactions, which have attracted considerable interest but until now have resisted clarification.¹⁰

We have found phenyl cations to be voracious electrophiles, attacking sigma- as well as pi-bonds and nonbonding electrons.

Reactions of $C_6H_5^+$ with methane produce both $C_7H_9^+$ and $C_7H_7^+$. Thus even when a fragmentation channel exists simple addition is observed, as with H_2 . Such simple addition reactions are rather unusual at the low pressures (10^{-5} to 10^{-6} torr) of the icr experiments since the exothermicity of the reaction must appear as internal energy of the adduct.

The principal reaction of $C_6H_5^+$ with ethane is the acquisition of two hydrogens, which can be formulated as:

With ethylene both hydrogen transfer and addition occurs:

An interesting reaction takes place with cyclopropane in which a formal transfer of methylene occurs:

While the details of these interesting reactions remain to be clarified, it appears that phenyl cations in the gas phase behave like excited highly electrophilic carbenes with an empty sigma-orbital instead of the empty pi-orbital usual for lowest singlet carbenes.

Dr. Michael Sefcik and Professor Jay Henis of Monsanto helped Dr. Speranza with these experiments.

Silylene reaction studies.

For the purpose of detecting silylene intermediates in the reactions of recoiling silicon atoms, and because of their intrinsic interest, as much as possible is being learned about the reactions of silylene with various substrates. These substrates can be employed in recoil reaction systems to search for their silylene adducts.

Having found that SiH_2 adds efficiently to butadiene²⁻⁴ and having demonstrated that the addition mechanism is not a concerted 1,4-cycloaddition^{3,11} we have now obtained evidence that silacyclopropanes intervene as reaction intermediates. This conclusion has been derived from reaction studies of silylenes with cyclic dienes.⁵

While SiH_2 and SiCl_2 give only the conjugated silacyclohexadiene upon addition to cyclopentadiene,

we have found that dimethylsilylene gives both conjugated and unconjugated adducts:

This result is consistent with a silacyclopropane intermediate, since pyrolysis of the all-carbon analog gives both cyclohexadienes,¹² via a biradical intermediate, in a ratio similar to that of the silacyclohexadienes.

Therefore it is likely that silacyclopropane formation followed by homolytic cleavage of the strained carbon-carbon bond occurs during dimethylsilylene addition:

The case for a silacyclopropane intermediate is most eloquently made by the finding of 3,3-dimethyl-3-sila-1,4,6-heptatriene as a product from the addition of dimethylsilylene to 1,3-cyclohexadiene. The following mechanism is proposed.

The other product of this reaction 7,7-dimethyl-7-silanorbornene, the first bicyclic silylene adduct reported, may - but need not - also arise via the silacyclopropane intermediate.

The lack of a nonconjugated silacyclohexadiene product from SiH_2 (and SiCl_2) and cyclopentadiene has prompted a search for the "missing" products, which might include silabenzene.

The experiments of this section have been carried out by Mr. Conlin and Mr. Hwang.

Thermal evaporation of germanium atoms.

The reaction of thermally evaporated germanium atoms with trimethylsilane, briefly reported in the last progress report,³ has been carefully studied and a communication describing the results written.¹³ Isolated yields of 1 to 3% of a new compound bistrimethylsilylgermane have been obtained.

This result is significant because "double insertion" by thermally evaporated germanium atoms indicates that thermally evaporated and nucleogenic germanium atoms undergo at least some reactions in common. A second report has appeared of a reaction of thermally evaporated germanium atoms in which the lack of observed double insertion was interpreted as indicating differences in electronic and kinetic energy between thermal and nucleogenic germanium atoms.¹⁴ Clearly such a distinction is not valid, as we have pointed out.¹³

Reactions of thermally evaporated germanium atoms with butadiene have been studied, but thus far only polymeric products have been obtained.

A higher temperature crucible and heater system incorporating a much larger transformer has been installed to permit efficient thermal evaporation of silicon atoms.

The experiments of this section were carried out by Mr. Conlin and Mr. Lockhart.

Study of silyl radicals by electron spin resonance spectroscopy.

Progress has been made toward solving the problem of generating silicon-centered free radicals conjugated with an aromatic ring or other pi-electron system capable of providing a direct measure of silicon-carbon pi-overlap. The extent of overlap can be readily deduced from the spin distribution which can in turn be derived from the hyperfine coupling constants taken directly from electron spin resonance spectra.

When fluid mixtures of tertiary butyl peroxide, benzene and trimethylsilane are irradiated with ultraviolet light in the cavity of an esr spectrometer, the only signal observed is that from the adduct of trimethylsilyl radical and benzene which results from the following reaction sequence:

While the addition of free radicals to benzene has long been proposed to account for the products of radical substitution reactions,¹⁴ this is the first time that a cyclohexadienyl radical has been directly observed spectroscopically under reaction conditions. A high yield of trimethylsilylbenzene was isolated as the reaction product. This esr technique can be employed to study the kinetics of cyclohexadienyl radical reactions.

This result makes it clear that it will be difficult to observe in solution aryl- or vinylsilyl radicals generated by hydrogen abstraction from silanes because the silyl radicals will immediately undergo addition to their unsaturated precursors thus reducing the radical lifetimes drastically. This difficulty can perhaps be overcome with the submicrosecond

time resolution afforded by a laser flash photolysis apparatus. Another solution is to employ a matrix isolation method.

Therefore we have begun working on the formation of phenyl and vinyl-silyl radicals under conditions such that the radicals will not be consumed rapidly.

We have chosen to employ the adamantane matrix method of Wood, which has been so successful for the preservation of organic radicals for spectroscopic observation.¹⁵

We have succeeded in observing well resolved spectra of trimethylsilyl radicals in an adamantane matrix - the first time that a silicon-centered radical has been observed in an adamantane matrix. From phenylsilane irradiated with X-rays in an adamantane matrix, a complex but poorly resolved esr spectrum was obtained which may be due to the desired phenylsilyl radical. The extent of stabilization of radicals in the interstices of adamantane crystals and the spectral resolution achieved for the esr signals both depend critically on the size of the radical molecule. It seems likely that a smaller radical than $\phi\text{SiH}_2\cdot$ may be observed more readily with resolution sufficient to map a spin distribution. Smaller radicals of interest are $\text{CH}_2=\text{CHSiH}_2\cdot$ and $\text{CH}_2=\text{CHSiMe}_2\cdot$.

Recently the triphenylgermyl radical has been observed, and its esr spectrum indicates considerable germanium-carbon π -overlap.¹⁶

We have completed and written up for publication Dr. Choo's experiments¹⁷ on a phase-shift method for measuring the rate of hydrogen abstraction from trimethylsilane by tertiary butoxy radicals.¹⁸ The important contribution is the measurement of a reaction rate for a free radical which could not be directly detected. The rate measurement was accomplished by measuring the

phase-shift between the product radical from the t-BuO $\cdot$ reaction and the square-wave modulated light source employed to produce the t-BuO $\cdot$ radicals.

The experiments of this section were carried out by Maurizio Speranza.

Study of abstraction of moieties other than hydrogen by recoiling silicon atoms.

The necessity of training new undergraduate research assistants in the past year has limited the progress made in this area.

A successful synthesis on a preparative scale of 1,2-dimethyldisilane has been developed.

The dimethyldisilane is required as a precursor to methylsilylene MeSiH: which will be employed in the synthesis of authentic materials required for the identification of products formed by the abstraction of methyl groups by recoiling silicon atoms. A typical synthesis is:

The experiments of this section were carried out by Maurizio Speranza.

PERSONNEL

Dr. Maurizio Speranza, who joined our group June 1, 1974, continued his experiments until the end of May, 1975. From June 1, 1974 to November 30, 1974 he was paid by the Italian National Research Council with a supplement from Washington University. From December 1, 1974 to May 30, 1975 his salary as a postdoctoral research associate came from Contract No. E(11-1)-1713. He contributed widely to our research effort, carrying out hot atom and free radical experiments as well as studying ion-molecule reactions.

Dr. Michael Sefcik, a former postdoctoral research associate, has continued active collaboration on ion-molecule reaction studies as has Dr. Jay Henis, both at the Monsanto Company

Mr. Hwang and Mr. Conlin continue their fruitful graduate studies and Mr. Roy Lewis has begun graduate work studying a chemical method for generating carbon atoms. He is also studying silyliminamino radicals by esr spectroscopy, looking for a new measure of silicon participation in pi-electron delocalization.

Mr. Barry Mizes, an undergraduate research assistant, decided to seek early admission to medical school and could not continue his research duties. Two new undergraduate research assistants, Mr. Bruce Cohen and Mr. Stephen Lockhart, began work in the Spring and have already made research contributions. They have been trained by Dr. Speranza, Mr. Hwang and Mr. Conlin, as well as by the principal investigator.

Dr. Joseph Patane, Ph.D. 1975, Wayne State University, is joining us at the end of August, 1975. His background in ion-molecule reactions and gas kinetics is perfect for pursuing the goals of this research project.

PUBLICATIONS

Five papers have appeared in the last twelve months:

1. COO-1713-42 "Hydrogen Elimination from Carbon-Silicon Ion Molecule Reaction Intermediates" by J. M. S. Henis, G. W. Stewart and P. P. Gaspar, J. Chem. Phys., 61, 4860 (1975).
2. COO-1713-45 "Organosilicon Iminamino Radicals from the Addition of Silyl Radicals to Diphenyldiazomethane" by Peter P. Gaspar, Chi-Tang Ho and Kwang Yul Choo, J. Amer. Chem. Soc., 96, 7818 (1974).
3. COO-1713-46 "Stereochemistry of a Silylene Addition Reaction" by Peter P. Gaspar and Rong-Juh Hwang, J. Amer. Chem. Soc., 96, 6198 (1974).
4. COO-1713-47 "The Methanium Ion, CH_5^+ . Evidence for the Structure of a Nonclassical Ion from Reaction Studies by Ion Cyclotron Resonance Spectroscopy" by Michael D. Sefcik, Jay M. S. Henis, and Peter P. Gaspar, J. Chem. Phys., 61, 4321 (1974).
5. COO-1713-48 "Silanium SiH_5^+ . The Protonation of Silane and the Chemistry of Silanium Ions Studied by Ion Cyclotron Resonance Spectroscopy" by Michael D. Sefcik, Jay M. S. Henis and Peter P. Gaspar, J. Chem. Phys., 61, 4329 (1974).

Three papers are in the press:

1. COO-1713-34 "Inorganic Hot Atom Chemistry in Gaseous and One-Component Liquid Systems" by Peter P. Gaspar and Michael J. Welch, Nuclear Transformations in Solids, G. Harbottle and A. G. Maddock, editors, North Holland, Amsterdam, in the press.
2. COO-1713-37 (revised) "Rates of Reaction of Hydrogen Atoms with Silane and Germane" by Kwang Yul Choo, Peter P. Gaspar and A. P. Wolf, J. Phys. Chem., in the press.

3. COO-1713-51 "Silylene Addition to Cyclopentadiene and 1,3-cyclohexadiene. Evidence for the Addition Mechanism" by Rong-Juh Hwang, Robert T. Conlin and Peter P. Gaspar, J. Organometal. Chem., in the press.

Two additional papers have been submitted for publication.

1. COO-1713-56 "The Rate of Hydrogen Abstraction from Trimethylsilane by Tertiary-Butoxy Radicals Measured by an Electron Spin Resonance Phase Shift Technique" by Kwang Yul Choo and Peter P. Gaspar, submitted for publication to J. Organometal. Chem.
2. COO-1713-57 "The Reactions of Germanium Atoms with Trimethylsilane" by Robert T. Conlin, Stephen H. Lockhart and Peter P. Gaspar, submitted for publication to J. Chem. Soc., Chem. Comm.

STATEMENT OF EFFORT

During the preceding twelve months the principal investigator has devoted approximately 25% of his time during the academic year to this project and 100% of three summer months. He also continued as a research collaborator at the Brookhaven National Laboratory.

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