

PROGRESS REPORT

August 31, 1970

REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

MASTER

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In the last year considerable progress has been made toward the basic goals of our research program: 1. Elucidation of the chemistry of recoiling silicon and germanium atoms and the manner in which their reactions take place, that is the reaction mechanisms; 2. Determination of the vibrational excitation and rates of rearrangement of reaction products; and 3. Exploration of the reactions of atomic silicon and germanium with a variety of reaction substrates.

A greatly improved personnel situation has enabled us to make strides forward in all aspects of the research program. Dr. Peter Markusch, a postdoctoral research associate from Göttingen arrived in November, 1969 and has made important contributions to the research effort. A first-year graduate student, Mr. Kwang Yul Choo, joined the research group in May, 1970 and has already carried out successful experiments described in this report. A new undergraduate research technician, Mr. Dewey Holten joined the group in April, 1970 and has worked full time during the summer. Both he and Mr. James Frost, an undergraduate beginning his fourth year on this project will continue their research during the academic year 1970-71.

The following summary of the research accomplishments of the past year is somewhat lengthier than previous progress reports. The increased volume of effort has led to a large body of knowledge which has not thus far appeared in print. In addition to the preprints enclosed with this report, two full papers are in preparation on the reactions with silane-disilane mixtures and with alkanes of silicon atoms recoiling from the transformation $^{31}\text{P}(n,p)^{31}\text{Si}$.

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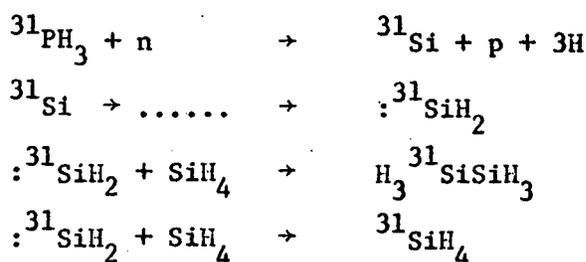
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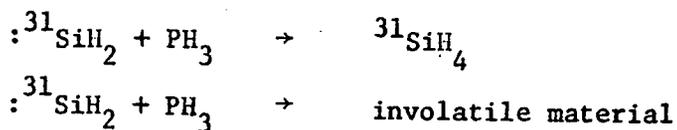
The principal efforts of the last year have centered on the reaction mechanisms of recoiling silicon atoms from the transformation $^{31}\text{P}(n,p)^{31}\text{Si}$ in systems consisting of phosphine, silane and disilane. The reactivity of silicon atoms toward carbon-hydrogen bonds has been profitably reexamined. Moderator studies on the energies at which primary reactions of recoiling silicon atoms take place have been greatly extended. The kinetics of silyl radical reactions have been studied both by steady state photolysis and by a newly developed technique combining flash photolysis with electron spin resonance spectroscopy. Silicon and Germanium atoms have been generated in a flow system and detected by atomic absorption spectroscopy.

A. Reactions of Recoiling Silicon Atoms with Phosphine, Silane and Disilane

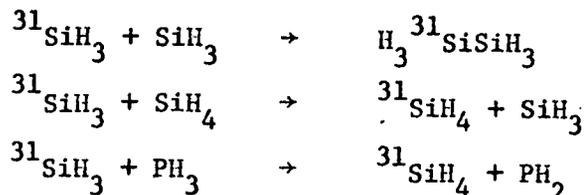
A complete picture of the reactions in phosphine-silane mixtures of silicon atoms produced by the nuclear transformation $^{31}\text{P}(n,p)^{31}\text{Si}$ is emerging for the first time from current experiments on phosphine-silane-disilane mixtures. The nature of the products (including a product newly discovered) and the selectivity among substrates have stimulated a unified hypothesis for the whole reaction sequence from the recoiling atom to the stable end products.

Results obtained in the last few months have confirmed the reaction scheme previously proposed for the product determining steps and have provided insight into the primary reaction processes of recoiling silicon atoms. Previously the formation of disilane $\text{H}_3^{31}\text{SiSiH}_3$ and silane $^{31}\text{SiH}_4$ from fast-neutron irradiation of phosphine-silane mixtures has been rationalized by proposing a set of product-determining steps involving the reactive intermediate silylene: $^{31}\text{SiH}_2$ thought to be the product of primary silicon atom reactions.





An alternative mechanism for the formation of disilane and silane, rendered unlikely but never previously disproved, involves the reaction of radioactive silyl radicals $^{31}\text{SiH}_3$ with nonradioactive silyl radicals, silane or phosphine respectively.



The nonradioactive silyl radicals required by this latter mechanism could be formed from silane by radiation damage. The steps involving silyl radicals had been rendered unlikely, however, by the failure of scavengers to affect product yields.

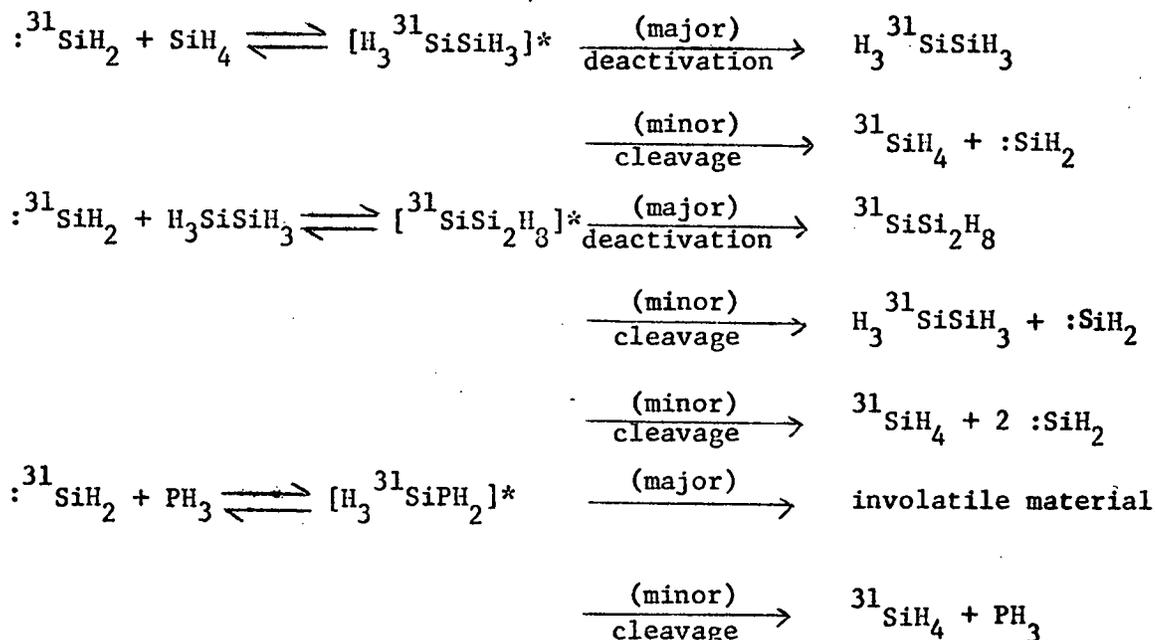
We have now obtained further evidence which confirms the intermediacy of $:^{31}\text{SiH}_2$ from the fast-neutron irradiation of phosphine-disilane mixtures. In this system the insertion of $:^{31}\text{SiH}_2$ into silicon-hydrogen bonds can be distinguished from the coupling of $^{31}\text{SiH}_3$ with the debris from radiation damage. Not only is the first reaction scheme confirmed, but the results suggest a more complete formulation.

If radiation damage were to occur in the phosphine-disilane system, SiH_3 would be formed by Si-Si scission as well as SiH_2SiH_3 by Si-H scission. Thus if $^{31}\text{SiH}_3$ were an important intermediate, radical coupling would lead to the formation of significant amounts of $\text{H}_3 ^{31}\text{SiSiH}_3$ as well as $\text{H}_3 ^{31}\text{SiSiH}_2\text{SiH}_3$. If on the other hand, $:^{31}\text{SiH}_2$ is the predominant intermediate, the major product from phosphine-disilane mixtures should be trisilane $^{31}\text{SiSi}_2\text{H}_8$, formed by Si-H or Si-Si (vide infra) insertion.

It was found that only a small amount of $\text{H}_3 ^{31}\text{SiSiH}_3$ was formed compared with the major product $^{31}\text{SiSi}_2\text{H}_8$ from the reactions of recoiling silicon atoms in phosphine-disilane mixtures. This result is in accord with the intermediacy of $:^{31}\text{SiH}_2$ which inserts into the Si-H or Si-Si bonds of disilane to yield trisilane.

A complete mechanism for the product determining steps may now be written which accounts for the small amounts of both $^{31}\text{SiH}_4$ and $\text{H}_3 ^{31}\text{SiSiH}_3$ which are formed

from silane-disilane mixtures and the $^{31}\text{SiH}_4$ formed from phosphine-silane mixtures.



Similar thermal decompositions of disilane and trisilane to silylene have recently been suggested by several groups to explain the products and reaction kinetics of disilane and trisilane pyrolysis. Silylphosphine is known to give silane and phosphine on pyrolysis.

A clue to the nature of the primary reactions of recoiling silicon atoms came from reexamination of the phosphine-silane system. Trisilane $^{31}\text{SiSi}_2\text{H}_8$ was found as a minor product which had been previously overlooked. Trisilane cannot result from reaction of $:^{31}\text{SiH}_2$ with SiH_4 . The formation of trisilane can be understood, however, if a primordial step toward the production of $:^{31}\text{SiH}_2$ is the insertion of a silicon atom into an Si-H bond of silane. The resulting divalent species $\text{H}-^{31}\text{Si}-\text{SiH}_3$ may occasionally survive to take part in a second insertion forming trisilane, although its normal fate seems to be Si-Si bond scission. Whether decomposition of the initial insertion product gives $:^{31}\text{SiH}_2$ directly is not known, but a set of steps for the production of $:^{31}\text{SiH}_2$ may be written as follows:



This primary reaction scheme is plausible but speculative and remains to be tested. Nevertheless, it is clear that our understanding of the reactions of recoiling silicon atoms is progressing rapidly.

An interesting new aspect of the reactions of $^{31}\text{SiH}_2$ is the possible occurrence of insertion into silicon-silicon bonds. A remarkably high ratio of trisilane $^{31}\text{SiSi}_2\text{H}_8$ to disilane $\text{H}_3^{31}\text{SiSiH}_3$ is obtained from the fast-neutron irradiation of phosphine-silane-disilane mixtures. Disilane appears to be 4.9 ± 1.9 times as reactive as silane toward $^{31}\text{SiH}_2$. A reactivity ratio of 1.5 is expected, based on the number of available Si-H bonds, if the Si-H bonds in silane and disilane are equally reactive. Thus it is clear the either the Si-H bonds of disilane are considerably more reactive toward insertion by $^{31}\text{SiH}_2$ than are the bonds of silane, or $^{31}\text{SiH}_2$ is undergoing insertion into the Si-Si bond of disilane to form $\text{H}_3\text{Si}^{31}\text{SiH}_2\text{SiH}_3$ as well as $\text{H}_3^{31}\text{SiSiH}_2\text{SiH}_3$ by 'normal' Si-H insertion.

Insertion into Si-Si bonds is a rather novel reaction, and is being investigated carefully. The work in this section has been carried out by Dr. Markusch.

B. Reactions of Recoiling Silicon Atoms with Phosphine-Alkane Mixtures

The reactivity of recoiling silicon atoms toward carbon-hydrogen bonds has been reexamined in detail, and it is concluded that C-H bonds are reactive toward recoiling silicon atoms or their primary products. Dr. Markusch and Mr. Holten carried out these experiments.

Addition of alkanes (CH_4 , C_2H_6 , C_3H_8 , and $(\text{CH}_3)_3\text{CH}$) to phosphine prior to irradiation with fast neutrons does not lead to new products other than $^{31}\text{SiH}_4$ which is obtained from pure phosphine. The yield of $^{31}\text{SiH}_4$ is not affected by the presence of even 50% alkane. On this basis alone, alkanes would be regarded as being inert toward recoiling silicon atoms.

On the other hand, when alkanes are compared with known inert moderators such as neon, a new factor emerges. Neon and other moderators reduce the product yields

from hot-atom reactions by removing energy from recoiling atoms in non-reactive collisions. Thus deactivation to less reactive thermal atoms is enhanced relative to reactions at high kinetic energies. Alkanes have been found to be less efficient moderators than neon, nitrogen and perfluoroethane, a result hardly possible if the role of alkanes is merely to accept kinetic energy from the recoiling atom. That the yield of $^{31}\text{SiH}_4$ is higher from phosphine-ethane mixtures than from mixtures of phosphine with neon, nitrogen or perfluoroethane suggests that alkanes may serve as reactants as well as moderators.

The addition of silane to phosphine-ethane and phosphine-neon mixtures prior to neutron irradiation leads to identical product yields from the two mixtures. This indicates that ethane is very much less reactive chemically than silane toward the recoil species. Whether ethane reacts directly with the recoiling silicon atoms or instead with a primary intermediate remains to be determined.

As expected from a model in which ethane and silane compete for a reactive intermediate, and ethane also exerts a moderator effect, decrease in the silane concentration increases the product yields from phosphine-silane-ethane mixtures when compared with phosphine-silane-neon mixtures.

C. Moderator Studies

Neon and argon had already been shown to exert a moderator effect on the reactions of recoiling silicon atoms in research previous to the current period. In the past year these experiments have been extended by Dr. Markusch and Mr. Holten to other moderators over a wider range of moderator pressures.

It has been found that neon, nitrogen, hexafluoroethane and argon are all effective moderators for recoiling silicon atoms. The results are in accord with moderator studies with other hot atoms. While earlier experiments with silicon indicated an exaggerated moderator effect, it is now clear that silicon atoms are subject to a typical moderator effect which indicates that their primary reactions

occur at high kinetic energies. Results with individual moderators are being analyzed using the Wolfgang-Estrup kinetic model.

An interesting facet of the moderator studies is that one product from phosphine-silane mixtures $^{31}\text{SiSi}_2\text{H}_8$ remains constant or increases slightly in yield while the yields of two products $^{31}\text{SiH}_4$ and $\text{H}_3^{31}\text{SiSiH}_3$ decrease with increasing moderator pressures. This suggests either a precursor of lower energy for trisilane, or that collisional deactivation of a vibrationally excited intermediate such as $\text{H-}^{31}\text{Si-SiH}_3$ is necessary for trisilane formation. Detailed comparison of different moderators and experiments at varying total pressures in the absence of moderator will resolve this question.

D. Kinetics of Silyl Radical Reactions

Study of the ground state chemistry of silyl radicals has been undertaken as part of a program in which the probable reactive intermediates in the reactions of recoiling silicon and germanium atoms are generated individually and their reactions examined under conditions similar to the recoil reactions.

Various silyl radicals ($(\text{CH}_3)_3\text{Si}$, $(\text{CH}_3)_2\text{SiH}$, CH_3SiH_2 , SiH_3 , $\phi_3\text{Si}$) have been generated by hydrogen abstraction, a method discovered by Krusic and Kochi. Radicals are produced by steady state in situ photolysis in the ESR spectrometer.



The triphenylsilyl radical is of interest in connection with theoretical questions about multiple bonding involving silicon. Its ESR spectrum is being analyzed to determine the unpaired electron densities at various atoms of the triphenylsilyl molecule.

Rates of reaction of silyl radicals are being measured by a newly developed flash photolysis technique. A xenon lamp is electronically pulsed with rise and fall times of ca. 10^{-5} sec. Concentrations of radicals produced in situ are repeti-

tively monitored by the ESR spectrometer at field strengths corresponding to maxima in the field-swept spectra obtained under steady-state illumination. The radical concentrations as a function of time are averaged and stored in a waveform eductor. Thus growth and decay curves for radicals may be directly obtained over intervals of 5×10^{-5} to ca. 10 seconds. The growth and decay curves are obtained directly on an oscilloscope or X-Y plotter, and rate constants are easily extracted. The apparatus has been found to be quite convenient for the study of silyl radical reactions whose half-lives are typically 10^{-4} seconds.

The modulated light source technique for studying short-lived radicals has several advantages over steady-state illumination. Not only are kinetic studies facilitated, but high quality ESR spectra of short-lived radicals can be obtained even in the presence of other radicals if the lifetimes of the radicals present differ. Development of this technique is entirely due to Professor S. I. Weissman. His assistance is gratefully acknowledged.

The dimerization of trimethylsilyl radicals is being studied over a wide temperature range. The kinetics of addition of silyl radicals to olefins is also under investigation. The work of this section has been carried out by Miss Allene Haizlip with the assistance of Dr. Haim Levanon, who works with Professor Weissman.

The techniques which are being developed in this laboratory for the study of silicon and germanium free radicals are capable of being extended to a variety of radical reactions of chemical and biological interest. The initiation of free radical polymerization, for instance, can be studied conveniently and in a more direct manner than by the conventional techniques of polymer kinetics.

E. Generation of Silicon and Germanium Atoms by Chemical Methods

Since August, 1969 there has been a collaborative effort together with Dr. A. P. Wolf of the Brookhaven National Laboratory on the generation of free atoms in a flow system and their detection by atomic absorption spectroscopy. I spent

five weeks at Brookhaven in July and August, 1969 working with Dr. E. Y. Y. Lam on the detection of carbon atoms formed from carbon suboxide by a microwave-sustained electrodeless discharge. Wolf and co-workers had already obtained chemical evidence for the formation of free carbon atoms in the system. Excited 1D and 1S carbon atoms were detected by atomic absorption spectroscopy at the characteristic wavelengths 1931 and 2479A respectively.

Dr. Lam carried on the work during the academic year in addition to full time teaching duties. This summer Dr. Lam resumed full-time work on the project and is assembling a combination of a vacuum-ultraviolet spectrometer and flow system capable of producing and detecting virtually any atom of interest in a variety of low-lying electronic states. In particular we will be able to study the reactions of ground state 3P carbon atoms with the new apparatus.

Mr. Kwang Yul Choo, a first year graduate student at Washington University, has begun study of the chemistry of chemically produced silicon and germanium atoms. In a two-week stay at Brookhaven in July, 1970, Mr. Choo was able, with Dr. Lam's assistance, to produce sizable concentrations of free silicon and germanium atoms in a helium stream by decomposition of various substrates (including silane and germane) in the electrodeless discharge. The principal investigator also spent a week at Brookhaven assisting Mr. Choo and Dr. Lam.

Conditions were optimized for the formation of ground state 3P silicon and germanium atoms which were detected by atomic absorption at the characteristic wavelengths 2516 and 2652A respectively. Excited silicon and germanium atoms were detected by emission spectroscopy on the plasmas in which they were formed. Study of the reactions of the ground state Si and Ge atoms is being carried out at Washington University using a flow system in which reactive substrates can be added to the gas stream downstream from the point at which the free atoms are generated.

The reactions of silicon atoms with silane and germane are already being investigated. Using this technique, reaction rates of any free atoms can be investigated in all low-lying electronic states whose chemical and physical lifetimes are sufficiently long for brief (ca. 10^{-3} sec.) survival after generation. Comparison of the flow system results with recoil experiments should lead to a better understanding of the variation of chemical reactivity with electronic state and kinetic energy.

F. Improved Instrumentation for Recoil Experiments

Two important developments have increased the range of accessible recoil experiments and also improved the accuracy of the results. First, a new irradiation cave was machined and placed into use. A three-inch circular orifice is now available interchangeably with the 1-1/4" irradiation port previously used. This permits a larger number of ampoules to be irradiated simultaneously or the use of larger ampoules, up to 16 mm. Thus an order of magnitude increase in the volume of reaction mixtures is possible, with a corresponding increase in the induced activity and sensitivity for minor products.

Second, the Nuclear Chicago flow counter with digital integrator and printer has been connected with a temperature-programmed vapor chromatograph. Both these pieces of equipment have been available since January, 1969, but their effective utilization required a new inlet system. Mr. Frost designed a heated stainless steel ampoule-breaking chamber and inlet manifold. This new gas inlet system permits the use of carriers with boiling points above ambient temperatures. The temperature programming feature facilitates analysis of a broad product spectrum from a single reaction mixture. The all-metal inlet manifold minimizes product loss prior to analysis. The combination of larger ampoules, metal inlet manifold and new counter have led to an improvement of 10^2 in counting rates for certain experiments. This will allow a much wider variation in reaction parameters than has previously been possible.

PUBLICATIONS

Only one paper has appeared in print thus far this year:

COO-1713-1515-15 "Preparation of Trisilane by the Schlesinger Method" by Peter P. Gaspar, Carl A. Lévy, and Gerald M. Adair, Inorganic Chemistry, 9, 1272 (1970).

A second paper is in the press:

COO-1713-18 "Silicon, Germanium and Tin Structural Analogs of Carbenes" by Peter P. Gaspar and B. Jerosch Herold, Carbene Chemistry second edition, W. Kirmse, ed., Academic Press, N. Y., in the press.

A preliminary communication has been submitted for publication to Chemical Communications on the work described in part A of this report:

COO-1713-16 "Reactions of Recoiling Silicon Atoms with Phosphine, Silane and Disilane" by Peter P. Gaspar and Peter Markusch, submitted to Chemical Communications.

A short paper about the production of carbon atoms and their detection by atomic absorption spectroscopy has been submitted for publication by Dr. A. P. Wolf:

"States of Atomic Carbon Produced in Decomposition of Organic Compounds in a Microwave Plasma" by Alfred P. Wolf, Ernest Y. Y. Lam and Peter P. Gaspar, submitted to the Journal of Physical Chemistry.

Two full papers are in preparation on the reactions of silicon atoms recoiling from $^{31}\text{P}(n,p)^{31}\text{Si}$ with silane-disilane mixtures and with alkanes. A communication is in preparation on the rates of reaction of trimethylsilyl radicals as determined by a flash photolysis ESR experiment.

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