PROGRESS REPORT

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REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

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In the last twelve months significant strides have been made toward the accomplishment of the research goals which we have set ourselves. These goals continue to be: 1. Elucidation of the chemistry of recoiling silicon and germanium atoms and the manner in which their reactions take place, that is to say the operative 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 substrates.

The summary of research accomplishments during the past year covers the following topics: a. Product-forming steps in the reactions of recoiling silicon atoms. b. Primary reactions of recoiling silicon atoms. c. Reactions of recoiling germanium atoms. d. Kinetics of silyl radical reactions and flow-discharge production of silicon, germanium and carbon atoms.

Product-forming steps in the reactions of recoiling silicon atoms.

For several years it has been clear that the most probable intermediates taking part in the product-forming steps of the reactions of silicon atoms recoiling from the $^{31}\text{P}(\text{n},\text{p})^{31}\text{Si}$ nuclear transformation in mixtures of

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phosphine and various silanes are silylene $^{31}\text{SiH}_2$ and silyl radicals $^{31}\text{SiH}_3$.

At least five mechanisms must be considered as a priori possibilities for the product forming steps:

- a. Abstraction of a single hydrogen atom by trivalent silicon.

- b. Abstraction of two hydrogens by a divalent silicon species.

- c. Insertion by silylene.

- d. Coupling of silyl radicals.

- e. Insertion by a silyl radical with hydrogen loss.

While paths a, d, and e all involving trivalent silyl radicals, had been previously rendered unlikely by scavenger experiments, some doubt has remained because of the unknown efficiencies of scavenger reactions. A year ago added evidence was obtained which precluded the operation of path d (see technical reports C00-1713-16 and C00-1713-20). Product

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studies carried out in recent months confirm the importance of $^{31}\text{SiH}_2$ as a reactive intermediate. Major products from recoiling silicon atoms in systems containing disilane and trisilane are the silylene insertion products. In the past year path b has been eliminated by the observation that 1,1,1-trimethyldisilane is a major product from fast neutron irradiation of trimethylphosphine-trimethylsilane mixtures in which there is no substrate with two labile hydrogen atoms. It had been previously demonstrated (see technical report C00-1713-20) that carbon hydrogen bonds do not contribute significantly to the formation of volatile radioactive products. Thus the formation of 1,1,1-trimethyldisilane is further evidence in favor of path c, silylene insertion.

Indirect evidence against path e comes from our kinetic studies of the rates of silyl radical reactions. Ring and coworkers have stipulated that the occurrence of path e (in the pyrolysis of silane) requires that the competing dimerization of silyl radicals be slow compared to the "insertion". We have found on the contrary that silyl radical dimerization is quite rapid, comparable to the dimerization of alkyl radicals (vide infra).

In the last year competition experiments have been carried out in ternary mixtures of phosphine, silane and disilane. Product yields have been quantitatively determined as a function of silane-disilane ratio, keeping the phosphine concentration constant. In this way a kinetic scheme has been confirmed in which a single reactive intermediate takes part in product-forming steps. The same set of rate constants accommodates the observed product yields whether or not scavenger nitric oxide is present.

This is taken as convincing proof that the product-forming reactive intermediate is not subject to scavenging by NO. The evidence taken together gives strong support to the postulate that silylene $^{31}\text{SiH}_2$ is the predominant product forming intermediate.

While insertion by silylene accounts for the formation of the major products from all silanes--the major products invariably contain one more silicon atom than the starting silane--the formation of lower homologs must also be rationalized. A year ago we proposed that the vibrationally excited silylene insertion products undergo unimolecular decomposition; e.g.,

In the past year we have found confirmation of this reaction scheme in the pressure dependence of product yields. As required by the scheme above, the yield of radioactive silane increases and the yield of radioactive disilane decreases with decreasing total pressure.

The arguments given here concerning the nature of the product forming steps in reactions of recoiling silicon atoms in mixtures of phosphine with silane, disilane and trisilane, together with the supporting data, have been submitted for publication as a full paper (COO-1713-24).

Further light on product forming steps has been provided very lately by the finding that silylphosphine $\text{H}_3 ^{31}\text{SiPH}_2$ is formed as a minor product in phosphine and phosphine-silane mixtures. Thus insertion by silylene

into phosphorus-hydrogen bonds also occurs. Silyl phosphines are very sensitive to radiation damage. Small yields of new products have also been obtained from phosphine-methane and phosphine-ethane mixtures. Their identification remains to be completed.

Careful confirmation of the role of silylene $^{31}\text{SiH}_2$ as a product-forming reaction intermediate is of continuing importance because the delineation of those products due to silylene reactions has allowed conclusions to be drawn concerning primary reactions of silicon atoms from those products not formed from silylene. These conclusions are summarized in the next section.

The experiments of this section were carried out by Dr. Markusch and Mr. Holten.

Primary reactions of recoiling silicon atoms. The first clue as to the nature of the primary reactions of silicon atoms recoiling from $^{31}\text{P}(n,p)^{31}\text{Si}$ in phosphine-silane mixtures was the detection of radioactive trisilane as a product formed in ca. 10% yield (see technical reports C00-1713-16 and C00-1713-20). Formation of trisilane can be most easily rationalized by two successive insertions into Si-H bonds. Clearly trisilane does not come from a silylene reaction.

In the past year evidence has been accumulated which supports this mechanism. The yield of trisilane has been found to increase with the square of the silane concentration (see technical report C00-1713-24).

In a pressure effect study the yield of trisilane has been found to decrease with decreasing total pressure. This is to be expected if the primary insertion product is vibrationally excited and can decompose if it is not collisionally deactivated.

The observed moderator effects are also in accord with this mechanism. There is a sharp decrease in the yield of radioactive disilane with the addition of a small amount of neon moderator to a phosphine-silane mixture. This large moderator effect at low moderator concentration suggests that the neon removes vibrational energy rather than translational energy, and that unimolecular dissociation of a primary intermediate is necessary for the formation of disilane. This primary intermediate is believed to be the insertion product of the recoiling silicon atom. The yield of trisilane increases as the disilane yield decreases, as predicted by the suggested mechanism. The mass balance suggests however that $\text{H} - {}^{31}\text{Si} - \text{SiH}_3$ has alternatives yet to be determined other than undergoing a second insertion to give trisilane or decomposing to the precursor of disilane.

Disilanylphosphine is another apparent reaction product found very recently in the silane-phosphine system. The proposed mechanism for trisilane formation can be extended to include insertion into phosphorus-hydrogen bonds thus predicting the formation of ${}^{31}\text{Si}$ -containing disilanyl-

phosphine and diphosphylsilane in addition to trisilane

The latter product has not yet been detected.

The evidence concerning primary reactions of recoiling silicon atoms in phosphine-silane mixtures will be incorporated in a full paper in the coming year. Dr. Markusch and Mr. Holten carried out these experiments.

Reactions of recoiling germanium atoms. The comparison of the recoil chemistry of germanium and silicon atoms is quite interesting. In general the chemistry of silicon and germanium compounds is similar. Since recoiling germanium atoms with high recoil energy can be produced from natural germanium by the nuclear transformation $^{76}\text{Ge}(n,2n)^{75}\text{Ge}$ a single component system from which high yields of volatile products are obtained can be used to study recoiling germanium atoms in the gas phase. (This is not the case for silicon atoms since pure phosphine gives only ca. 2% yield of $^{31}\text{SiH}_4$.)

In a preliminary communication two years ago (technical report COO-1713-8) it was reported that germanium atoms recoiling in pure germane

give radioactive germane and digermane as products while in germane-silane mixtures silylgermane is formed in addition to germane and digermane.

In the past year Mr. Frost has greatly extended our information about recoiling germanium atoms.

In addition to the radioactive germane and digermane previously observed as reaction products from pure germane, trigermane is also formed, and at quite high pressures a few percent normal tetragermane is also detected. The relative amount of trigermane increases with total pressure and the germane yield decreases.

In a series of scavenger experiments it was shown that the presence of 5% nitric oxide reduces all product yields from pure germane by 25%. Product yields decrease 50% in the presence of 5% ethylene and are unaffected by the presence of 5% methane.

It is very interesting to find that germane-silane mixtures give, in addition to the radioactive products previously reported: germane, germysilane and digermane the newly discovered products GeSi_2H_8 , Ge_2SiH_8 and trigermane. The yields of all products have been determined as a function of the germane-silane ratio.

The available data for the reactions of recoiling germanium atoms suggest an overall reaction mechanism very similar to that for recoiling silicon atoms. In particular, $^{75}\text{GeH}_2$ seems to be an important product-forming intermediate, and insertion by germanium atoms into Ge-H and Si-H bonds appears to be the dominant primary reaction. The significant yields of trigermane and the 'crossed-insertion products' Ge_2SiH_8 and GeSi_2H_8 are in accord with this double insertion hypothesis.

With the additional information that trigermane is the major

radioactive product from digermane, accompanied by small amounts of germane, digermane and normal-tetragermane we propose that decomposition of vibrationally excited insertion products plays an important role in the chemistry of recoiling germanium as well as silicon atoms. Thus we propose the following mechanism, many details of which remain to be confirmed.

A full paper on the reactions of recoiling germanium atoms is in preparation.

Kinetics of silyl radical reactions and the production of silicon, germanium and carbon atoms in a flow discharge system. The flash-photolysis-ESR technique described in the 1970 progress report (COO-1713-20) has been applied to the dimerization of trimethylsilyl $(\text{CH}_3)_3\text{Si}\cdot$ and silyl $\cdot\text{SiH}_3$ radicals and to the addition of silyl radicals to ethylene. The dimerization of trimethylsilyl radicals has been studied over a temperature range of nearly 200° (from -160 to $+30^\circ\text{C}$). That the disappearance of $(\text{CH}_3)_3\text{Si}$ is a clear second-order process was demonstrated by the lack of dependence of the second-order rate constant on the radical concentration nor on the intensity of the photolysis light source. Silyl radicals also disappear in a second-order process in a solution consisting of a mixture of silane and ethane. The rapid dimerization of SiH_3 tends to cast doubt on the reaction, proposed by other workers, in which silyl radicals react with silane to give disilane and a hydrogen atom. This latter reaction is however believed to take place in the gas phase at high temperatures-conditions very different from those of our experiments.

The rate of addition of silyl radicals to ethylene is being studied in solutions consisting of mixtures of silane, ethane and ethylene. In a mixture of 60% ethylene and 40% silane, addition is sufficiently rapid

to completely suppress dimerization of silyl radicals. By careful adjustment of the concentrations of silyl radicals and ethylene, rates of addition can be measured. It is already clear that ethylene is a highly efficient scavenger of silyl radicals.

Work has progressed both at Brookhaven and in Saint Louis in the generation of silicon, germanium and carbon atoms in a discharge-flow system. Ground state silicon and germanium atoms have been detected by atomic absorption spectroscopy downstream from the discharge in which they were formed. When silane is introduced into a helium stream containing silicon atoms produced in the microwave sustained discharge, disilane is produced. It was proved that the disilane is due to the reactions of silicon atoms and not due to reactions of the hydrogen atoms also produced. Thus it appears that the flow-system experiments will provide additional information which will shed light on the reactions of the atoms which we are studying in recoil experiments. Preliminary observations on the production of silicon and germanium atoms are contained in a communication which is in the press (technical report COO-1713-22).

While the observation of excited state 1D and 1S carbon atoms from the decomposition of carbon suboxide in a microwave discharge was reported last year, work is continuing on the detection of ground state 3P carbon atoms. A discharge flow system incorporating a vacuum monochromator has been assembled with an experimental hollow-cathode lamp as the source of the $1657 \text{ \AA}$ carbon resonance lines.

PERSONNEL

The personnel situation has continued to be very favorable. After a productive stay of 18 months in Saint Louis, Dr. Peter Markusch returned to Germany in May. Mr. John J. Frost was graduated summa cum laude and was also awarded the John Sowden Memorial Prize as the outstanding undergraduate chemistry student at Washington University. Mr. Frost worked very productively for four years on this project. The tradition of outstanding undergraduate research effort in our group is being maintained by Mr. J. Dewey Holten III who is beginning (as a junior) his second year on the project. Mr. Kwang Yul Choo, beginning his third year of graduate work is also continuing his research. Miss Quida Draine a second year graduate student worked during the academic year on a new chemical method for the generation of carbon atoms. In August a new postdoctoral research associate begins working on the reactions of recoiling silicon and germanium atoms. Dr. Gerald Stewart received his Ph.D. at the University of Idaho having written his dissertation on the reactions of recoiling phosphorus atoms. Dr. Stewart arrived in Saint Louis in June and has been an instructor teaching an advanced physical chemistry in the summer session while planning his research program.

PUBLICATIONS

Two papers have appeared in print in the last twelve months:

1. COO-1713-16 "Reactions of Recoiling Silicon Atoms with Phosphine, Silane, and Disilane" by Peter P. Gaspar and Peter Markusch, Chemical Communications, 1970, 1331.
2. From the Brookhaven National Laboratory: "States of Atomic Carbon Produced in Decomposition of Organic Compounds in a Microwave Plasma" by Ernest Y. Y. Lam, Peter Gaspar and Alfred P. Wolf, Journal of Physical Chemistry, 75, 445 (1971).

There are two papers in the press:

1. COO-1713-18 "Silicon, Germanium and Tin Structural Analogs of Carbenes" by Peter P. Gaspar and B. Jerosch Herold, Carbene Chemistry, second edition, N. Kirmse, editor, Academic Press, N. Y., in the press (publication, delayed by the British postal strike, is due immediately).
2. COO-1713-22 "A Flow Method for the Study of Silicon and Germanium Atom Reactions by Direct Spectroscopic Observation" by Peter P. Gaspar, Kwang Yul Choo, Ernest Y. Y. Lam and Alfred P. Wolf, Chemical Communications, in the press.

A full paper has been submitted for publication to the Journal of Physical Chemistry on the product forming steps in recoil silicon reactions: COO-1713-24 "The Chemistry of Recoiling Silicon Atoms. V. Product-Forming Reactions in $\text{PH}_3\text{-SiH}_{n+2}$ Mixtures" by Peter P. Gaspar, Peter Markusch, J. Dewey Holten III, and John J. Frost, submitted to the Journal of Physical Chemistry.

In addition to the publications listed above a manuscript COO-1713-21 was prepared for the invited paper presented by the principal investigator at the 1971 Nuclear Award Symposium of the American Chemical Society held on March 29-30 in Los Angeles during the national ACS meeting. The talk was entitled "Silicon Atoms-Recoil Chemistry".

STATEMENT OF EFFORT

During the preceding twelve months the principal investigator has devoted approximately 30% of his time during the academic year to this project and expects to do so for the three months remaining of the current term of this research agreement. 100% of the three summer months have been devoted to this project by the principal investigator.