MASTER

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REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

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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. Silicon free radical chemistry; d. The role of ionic reactions in the chemistry of recoiling silicon atoms.

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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.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;
- b. Thermally induced silylene and germylene reactions;
- c. Silicon free radical chemistry;
- d. The role of ionic reactions in the chemistry of recoiling silicon atoms.

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

The importance of studying the recoil-induced reactions of polyvalent atoms is evident from the observation that the silicon and germanium atoms recoiling from the $^{31}\text{P}(\text{,np})^{31}\text{Si}$ and $^{76}\text{Ge}(\text{n,2n})^{75}\text{Ge}$ nuclear transformations behave quite differently from the thermally generated atoms.⁴⁻⁶ In reactions with silanes and germanes the major products from the recoiling atoms are the next higher homologs:^{7,8}

Thermally generated silicon and germanium atoms, in contrast, give as pre-dominant products of reaction with Si-H and Ge-H bonds consecutive insertion products, also found but in low yields, in recoil reactions.⁹⁻¹¹

We have suggested that the difference between the reactions of recoiling and thermal silicon and germanium atoms in the systems studied is primarily due to the formation of silylene $^{31}\text{SiH}_2$ and germylene $^{75}\text{GeH}_2$ in the recoil systems, these reactive intermediates then undergoing insertion into Si-H and Ge-H bonds.⁴⁻⁸

It is known that thermally generated SiH_2 inserts efficiently into Si-H and Ge-H bonds,¹² and that GeH_2 inserts into Ge-H bonds.^{13,14} A further observation consistent with a silylene intermediate in the recoil reactions is the formation, in low yield, of an adduct with butadiene, 1-silacyclopent-3-ene.^{6,15-17} This product has been obtained in 50% yield from addition of thermally generated silylene to butadiene,^{6,16}

While qualitative criteria for participation by ${}^{31}\text{SiH}_2$ and ${}^{75}\text{GeH}_2$ intermediates have been convincingly met, there have been recent indications that the intermediates in the recoil systems differ markedly in their reactivity from thermally produced silylenes and germylenes.

The relative reactivity of silane and butadiene toward the intermediate to which the ${}^{31}\text{SiH}_2$ structure has been assigned is 10:1 but toward thermally generated SiH_2 silane and butadiene are believed to be roughly equal in reactivity. Thermally generated silylene reacts with cyclopentadiene to produce 1-silacyclohexa-2,4-diene,¹⁸ but this product is not observed from recoiling silicon atoms.^{5,6}

These observations would still be compatible with a ${}^{31}\text{SiH}_2$ intermediate if the selectivity of the silylene in the recoil systems is different from that of thermally generated silylene, which would be expected if the silylene intermediate in the recoil system reacted at high energy - either kinetic, electronic or vibrational. The comparison between the relative reactivity

of the intermediates in the reactions of recoiling silicon atoms with that of thermally generated silylene is complicated by the high temperatures (ca. 300° C) employed for the thermal reactions compared with the ambient temperature of reaction mixtures in the reaction studies.

We have therefore undertaken in the past year a series of experiments in which the relative reactivity of methylsilane and silane towards recoiling silicon atoms was determined. This pair of substrates was selected because their relative reactivity toward thermally generated SiH_2 has been carefully determined, including its temperature variation, by Paquin and Ring.¹⁹

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

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

In the narrow range of temperatures studied (246-287° C) the ratio of reactivities $k_1:k_2$ ranged from 0.97 to 1.3. Use of the activation parameters in an extrapolation to room temperature gave a predicted $k_1:k_2 = 0.051$ with an upper limit of 0.13.

We have found that variation of the $^{31}\text{SiH}_3\text{SiH}_2\text{CH}_3$ to $^{31}\text{SiH}_3\text{SiH}_3$ product ratio with the $\text{SiH}_3\text{CH}_3 : \text{SiH}_4$ substrate ratio in recoil experiments gives a relative reactivity of methylsilane to silane for the product forming intermediate of 1.34 ± 0.02 . This is an order of magnitude higher than that expected for $^{31}\text{SiH}_2$ in its ground electronic state at room temperature.

Thinking that this discrepancy may be due to excess energy we carried out an experiment to determine the effect of moderator on the competition ratio. In a series of moderator experiments on the reactions of recoiling silicon

atoms in binary phosphine-silane mixtures it was determined that the yield of disilane, the product attributed to $^{31}\text{SiH}_2$, does decrease significantly with increasing partial pressure of moderator, and that the effectiveness of the moderator in decreasing the yield is in accord with a simple hard sphere model such that the order of effectiveness is $\text{Ar} > \text{Ne} > \text{Kr} > \text{Xe}$. Thus excess kinetic energy is definitely required for disilane formation.

It was found however that argon moderator does not change the relative yields of $^{31}\text{SiH}_3\text{SiH}_2\text{CH}_3$ and $^{31}\text{SiH}_3\text{SiH}_3$ in competition experiments. Thus SiH_3CH_3 and SiH_4 compete for an intermediate that does not contain energy that is removable by argon moderator, and the selectivity ratio is not that expected for $^{31}\text{SiH}_2$.

Another possibility is that $^{31}\text{SiH}_2$ is an important intermediate, but is in an excited triplet electronic state rather than the singlet ground state. Therefore the effect of nitric oxide scavenger on the competition ratio was examined in the belief that NO could selectively scavenge triplet silylene, as proposed by Tang.¹⁷ It was found, however, that nitric oxide does not significantly alter the selectivity ratio of the intermediate in the recoil experiment for methylsilane and silane. Therefore if the extrapolated selectivity ratio for thermal silylene can be trusted, the product forming intermediate even in the presence of 90% moderator and scavenger designed to remove triplet SiH_2 is not thermalized ground state singlet SiH_2 . In the proposal for the next year experiments are described in which the remaining possibility for a silylene intermediate, vibrationally excited SiH_2 will be tested. The competition recoil experiments will also be repeated at the same high temperatures used for thermal SiH_2 to avoid extrapolation errors and to explore the temperature dependence of the selectivity ratio.

Other mechanisms have continued to be explored. Ionic intermediates

SiH_n^+ ($n = 0, 1, 2, 3$) have previously been considered,²⁰ but unequivocal evidence in their favor has not been found. In the reactions of recoiling silicon atoms with trimethylsilane, new evidence for ionic intermediates has been obtained in the past year. The yields from 1:1 mixtures of PH_3 and HSiMe_3 are in order of increasing vpc retention time as follows:

<u>Product</u>	<u>Absolute yield, %</u>
$^{31}\text{SiH}_4$	1.9
$^{31}\text{SiH}_3\text{CH}_3$	0.4
unknown	0.1
$^{31}\text{SiH}_3\text{Si}(\text{CH}_3)_3$	36.
$\text{CH}_3^{31}\text{SiH}_2\text{Si}(\text{CH}_3)_3$	10.
unknowns	5.
$(\text{CH}_3)_3\text{SiSiH}_2\text{Si}(\text{CH}_3)_3$	5.1
unknown	2.5

It is noteworthy that at least two products, $^{31}\text{SiH}_3\text{CH}_3$ and $\text{CH}_3^{31}\text{SiH}_2\text{Si}(\text{CH}_3)_3$, require methyl abstraction by a recoil species for their formation. Such methyl abstraction from methylsilanes has been found by Lampe and coworkers as an ion-molecule reaction²¹ but methyl abstraction is not known for neutral silicon atoms or radicals.

Another significant clue concerning the reactions of recoiling silicon atoms was obtained in the past year in a careful look at the high boiling products from recoiling silicon atoms and butadiene. The spiro-silanonadiene, which can only be due to two consecutive additions to butadiene has been

Unequivocally detected as a product, albeit at low yield.

The importance of this product, whose low yield prevented us from detecting it in earlier experiments,^{5,6} is that it proves that butadiene is capable of directly trapping recoiling silicon atoms.

In the reactions of recoiling germanium atoms the selectivity among reaction substrates also differs from that found in the thermally generated divalent species germylene GeH_2 . In mixtures of GeH_4 and SiH_4 or HSiMe_3 products are formed from insertion into Si-H as well as Ge-H bonds

but for thermally generated GeH_2 , Ge-H bonds are more than 100 times as reactive as Si-H bonds.¹³ In the recoil experiments trimethylsilane is in fact three times as reactive as germane.

We have carried out moderator experiments and found that Ne, Ar, and Kr (in increasing order of effectiveness) diminish the yield of digermane, and decrease the relative reactivity of the silanes. Thus a kinetically excited germanium recoil species is required for reaction with an Si-H bond and kinetic energy also enhances the reactivity with the Ge-H bond. A plateau value is reached for the digermane yield, and this suggests that two different processes contribute to digermane formation. The effect of xenon moderator is quite different however, causing virtually no decrease in the yields of digermane and silylgermanes. We attribute this to the neutralization of a germanium ion to a neutral excited germanium atom.

We have constructed a reaction scheme for the primary interactions at recoiling germanium atoms and ions that is compatible with all the observations. The scheme assigns the reactions in which silanes can compete with germanes to a kinetically excited germanium atom, possibly a triplet derived from a low energy germanium ion, while an electronically excited germanium atom gives rise to digermene, but not a germysilane. In this reaction sequence ground state germylene may participate and be the only precursor for digermene at high moderator.

The participation of ionic reactions in the recoil chemistry of germanium is rendered probable by the existence of a metastable state ^{75m}Ge 0.139 MeV above the ground state, and decaying to it with a 48 second half-life. This isomeric transition is likely to involve a considerable degree of internal conversion and formation of germanium ions by the Auger process. The details of this scheme are still being worked out.

The experiments of this section have been carried out by Dr. Siu-Hong Mo (recoiling silicon atom competition experiments), Adam Helfer (recoiling silicon atoms and butadiene) and Roger Woods (recoiling germanium atoms).

Thermally induced silylene and germylene reactions

The study of thermally generated reactive species in parallel with the investigation of chemistry of recoiling silicon and germanium atoms facilitates the identification of product forming intermediates in the recoil systems and permits the assessment of the effects of excess energy, spin state and charge on the reactivity of the recoil species. It is the knowledge that we have helped develop the reactivity of thermally produced silylene SiH_4 and germylene GeH_2 that has permitted the design of the recoil experiments described in the previous section for the detection of $^{31}\text{SiH}_2$ and $^{75}\text{GeH}_2$ intermediates. We have continued our studies of chemically generated silylenes and germylenes to increase our knowledge of these interesting species, to develop better reactions for their production, and to find new chemical trapping reagents for them.

In the past year we have produced a new precursor for dimethylsilylene, designed to give a higher molecular weight by product easily separated from low-boiling reaction products. We have used this precursor, 1,2-diethoxy-1,1,2,2-tetramethyldisilane for the improved preparation of a fascinating silylene adduct tetramethylsilacyclopentene, first prepared in our laboratory in 1976 and the first silacyclopentene ever obtained in stable form.²²

Use of this new dimethylsilylene precursor has led to the preparation of solutions containing as high as 30% of the thermally stable but air-, water-, and metal-sensitive silacyclopentene. Spectroscopic measurements on these solutions with the newly installed Chemistry Department JEOL FX-100 multi-nuclear Fourier transform nmr machine established the ^{29}Si chemical shift as

tion apparatus for the study of the reactions of thermally evaporated silicon and germanium atoms with cocondensed reaction substrates. The high temperatures required for evaporation of silicon (1600°C) and germanium (1400°C) dictate that efficient thermal shielding of the vapor source be employed, and for safety considerations a sturdy steel reaction container was needed. These requirements have been met in our new apparatus that should permit the evaporation of 100 mg silicon per hour with a geometry that should give high product yields.

The accompanying proposal explains the importance of our first target with the new apparatus, the reactions of silicon and germanium atoms with butadiene.

The experiments of this section have been carried out by Ms Cornett (tetramethylsilacyclopropene from dimethylsilylene), Mr. Chen (bis(trimethylsilyl)silylene), Mr. Ma (germylenes and thermal evaporation of Si and Ge) and Mr. Barzilai (synthesis of dimethylgermylene reaction products).

Silicon free radical chemistry

Two problems have received active attention in the past year: 1. The disproportionation of trimethylsilyl radicals; and 2. The effects of silicon substituents on the structure of iminamino radicals, a class of radicals discovered in our laboratory from addition of organosilyl radicals to diphenyldiazomethane.²⁵ We have completed our work on this latter problem.

We have found in the past year that trimethylsilyl radicals undergo disproportionation to a silaolefin in competition with radical recombination.²⁶

Formation of the silaolefin, a relatively new class of compound that is receiving considerable attention,²⁷ was confirmed by trapping with deuterated tertiary-butanol :

This discovery of the disproportionation of trimethylsilyl radicals resulted from our efforts to determine the source of the tert-butoxytrimethylsilane previously observed as a minor product in our kinetic study of the dimerization of trimethylsilyl radicals.²⁸

The importance of the newly found disproportionation reaction is that competition of disproportionation with the very rapid, nearly diffusion-controlled recombination reaction, requires that the disproportionation must have a very low activation energy, perhaps due to stabilization of the transition state by the incipient carbon-silicon pi-bond. Facile disproportionation of trimethylsilyl radicals may therefore be taken as indirect evidence for substantial pi-

bonding in the sila-olefin.

In the course of this study another new route to silaolefins was discovered:

In concluding our studies of the influence of silyl substituent on the structure of iminamino radicals,²⁹ several new iminamino radicals have been prepared in the last year. These are shown below, with their nitrogen hyperfine coupling constants.

$$a_{\text{N}} = a_{\text{N}'} = 10.35 \text{ gauss}$$

$$a_{\text{N}} = 7.0 \text{ gauss}$$

$$a_{\text{N}'} = 3.0 \text{ gauss}$$

In addition a specifically ¹⁵N labelled iminamino radical was prepared, whose unshared electron occupies a sigma-orbital.

For the all ¹⁴N-iminamino radical two different nitrogen hyperfine coupling constants of 9.0 and 17.6 gauss were determined. The labelling experiment allowed the assignment of the larger coupling constant to the ¹⁵N atom and thus the nitrogen that formally carries the unshared electron in this radical has the smaller coupling constant. These results suggest that the hybridization of the central nitrogen is sp² and the terminal nitrogen sp.

Thus hyperconjugation of the "filled" sp^2 atomic orbital on N_2 with the "half-filled" p-orbital on N_1 transfers spin density to N_2 and accounts for the larger coupling constant due to the spin density in the s-weighted orbital on N_2 . The smaller coupling constant for N_1 reflects the p-character of the orbital containing the unpaired electron. Thus we have the larger coupling constant associated with the lower spin density.

The structure of pi-iminamino radicals is believed to involve sp^2 -hybridization for both nitrogens, with bulky substituents altering the twist angle about the N-N bond.

We feel that it is the electronic effects of substituents on $N-1$ that determine whether a particular iminamino radical will adopt a sigma- or a pi-electronic structure, but an interplay of several factors is indicated, including the delocalization of both the unpaired electron and the lone-pair on N_1 . The hyperfine coupling constants are very sensitive to the small twist-angle about the N_1-N_2 bond and these are determined principally by the bulk of the substituents at both N_1 and C.

The work of this section has been carried out by Ms. Becky Cornett (trimethylsilyl radical disproportionation) and Mr., now Dr. Roy Lewis (iminamino radical structure).

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

The ionization potential of atomic silicon (8.1 eV) is much lower than that of the reaction systems in which recoiling atoms are produced. Should they therefore reach thermal energies as positive ions $^{31}\text{Si}^+$, they would be consumed by ion-molecule reactions of high cross section more rapidly than they would be neutralized. We have found such reactions for thermal Si^+ at low pressure using ion cyclotron resonance spectroscopy,³⁰ and we also found a reaction sequence that could produce trisilane from Si^+ .²⁰ Thus ion-molecule reactions could contribute to the formation of products in the reactions of recoiling silicon atoms. Similar considerations suggest that ion-molecule reactions might also participate in the chemistry of recoiling germanium atoms.

Experiments designed to determine the extent to which ion-molecule reactions contribute to the formation of volatile products in the recoil systems have given ambiguous results. The addition of tertiary amines, substances with sufficiently low ionization potentials to neutralize ground state thermal $^{31}\text{Si}^+$ and $^{75}\text{Ge}^+$ ions has not reduced product yields except at very high amine concentrations. Therefore the participation of ground state thermal ions is not indicated.

In the past year, however several interesting new observations have been made that suggest the participation of ionic reactions.

The product formed in second highest yield (10%) in the reactions of recoiling silicon atoms in phosphine-trimethylsilane mixtures has been identified as 1,1,1,2-tetramethyldisilane, $(\text{CH}_3)_3\text{Si}-^{31}\text{SiH}_2-\text{CH}_3$. The importance of this product is that transfer of a methyl group must have occurred for its formation. Methyl group transfer from a methylated silane to a neutral silicon species is not known, but Lampe and coworkers have observed transfer of methyl groups to alkyl cations.²¹ It does therefore seem likely that nonthermal recoiling silicon ions do play a role in recoil reactions.

The tetramethyldisilane, a previously unknown compound, was identified by synthesis of a comparison sample. This long sought compound was prepared by alkylation of 1,1,1-trimethyldisilane with methyl lithium. This reaction was

adopted from a procedure discovered by Ring and coworkers.³¹

In the reactions of recoiling germanium atoms with germane - trimethylsilane and germane - tetramethylsilane mixtures, products have been found that are believed to be methylated germanes and digermanes. These too would suggest that ionic reactions contribute to product formation, and their identities will be determined by comparison with authentic samples.

In preliminary experiments on the reactions of recoiling silicon atoms in $\text{PH}_3\text{-CF}_4$ mixtures it appears that $^{31}\text{SiF}_4$ is formed and this too is more easily explained in forms of ionic rather than neutral reaction sequences.

Study of the following electron transfer reactions by ion cyclotron resonance spectroscopy verified that trimethylphosphine does indeed have a higher ionization potential (literature value 8.60 eV) than atomic silicon (8.15 eV). Since trimethylphosphine has a much lower ionization potential than phosphine PH_3 itself (10.0 eV) the lower yields of silicon recoil reaction products may be related to the occurrence of ion molecule reactions.

The experiments of this section were carried out by Dr. Mo (reactions of recoiling silicon atoms with trimethylsilane and synthesis of the tetramethyldisilane), Adam Helfer (reactions of recoiling silicon atoms with carbon-fluorine bonds) and James Dunbar (ion cyclotron resonance spectroscopy).

PERSONNEL

Dr. Siu-Hong Mo, an outstanding postdoctoral research associate joined this group in August 1978, having earned his Ph.D. at the University of California, Davis working under the direction of Professor John Root. Dr. Mo has been very successful in his first year and is going to continue for a second year. The Principal Investigator will give a paper based on Dr. Mo's work at the 10th International Hot Atom Chemistry Symposium, Loughborough University of Technology, September 2-7, 1979.

In May, 1979 Dr. Roy Lweis received his Ph.D., his dissertation describing the effects of silyl substituents on the structure of iminamino radicals. He has accepted a research position with DuPont in Wilmington, Delaware. Advanced graduate student Becky Cornett is completing her studies of the formation and reactions of tetramethylsilacyclopropene and on the disproportionation of trimethylsilyl radicals in the Fall of 1979.

Third year graduate students Eric Ma and Yue-Shen Chen are making solid contributions to the study of thermally generated germylenes and silylenes. Mr. Ma has designed and completed the supervision of the construction of a new apparatus for studying the reactions of refractory metal vapors and will use these for thermally evaporated silicon and germanium. Second year graduate student James Dunbar is continuing his study of ion molecule reactions by ion cyclotron resonance spectroscopy.

The undergraduate members of the group have continued to make first-rate contributions. Roger Woods, a junior, developed and carried out a number of experiments on the reactions of recoiling germanium atoms and the Principal Investigator will present our new proposals based on this work at the forthcoming Loughborough meeting. Adam Helfer, also a junior, has prime responsibility for the minicomputer interfaced with our radiochromatography apparatus and has

made important observations in his study of the addition of recoiling silicon atoms to butadiene and in the reaction of recoiling silicon atoms with C-F bonds.

The strength of the group working on this project in August, 1979 is one postdoctoral associate, four graduate students and three undergraduates. As promised in the last progress report, rapid progress is being made in all segments of this research.

STATEMENT OF EFFORT

During the preceding twelve months the Principal Investigator devoted approximately 25% of his time during the academic year to this project. Seven weeks in May and June of 1979 were spent in England. The rest of the summer was spent in the laboratory in St. Louis.

PUBLICATIONS

In the past twelve months four papers were published:

1. COO-1713-70, P.P. Gaspar and M.J. Welch, "Adendum to: 'Inorganic Hot Atom Chemistry in Gaseous and One-Component Liquid Systems,'" published with COO-1713-34 (same title), Chemical Effects of Nuclear Transformations in Inorganic Systems, G. Harbottle and A.G. Maddock, Eds., North-Holland, Amsterdam, 1979, Chapter 4, pp. 75-101
2. COO-1713-71, P.P. Gaspar, "Recent Advances in Silylene Chemistry, "Reactive Intermediates, Volume 1, M. Jones, Jr. and R.A. Moss, eds. Wiley, N.Y., 1978, Chapter 7, pp. 229-277.
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., 100, 6626 (1978).

4. 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," J. Phys. Chem., 182, 2633 (1978).

One paper has been submitted for publication:

1. COO-1713-82, Becky J. Cornett, Kwang Yul Choo and Peter Gaspar, "Disproportionation of Trimethylsilyl Radicals to a Silaolefine in the Liquid Phase," submitted for publication to J. Amer. Chem. Soc.

In addition the dissertation of Dr. Roy Lewis was completed: COO-1713-83, Roy Leon Lweis, Jr., "The Molecular and Electronic Structure of Iminamino Radicals," doctoral disseration, Washington University, May 1979.

Two contributed papers have been prepared for the Tenth International Symposium on Hot Atom Chemistry, Loughborough University of Technology, September 2-7, 1979 and will be read by the Principal Investigator: COO-1713-78, Roger P. Woods, Bruce H. Cohen and Peter P. Gaspar, "Primary Reactions of Recoiling Germanium Ions," and COO-1713-79, Siu-Hong Mo, J. Dewey Holten, III and Peter P. Gaspar, "Reactions of Recoiling Silicon Atoms with the Methylsilanes $H_n SiMe_{4-n}$." An invited lecture will also be presented at Loughborough: COO-1713-81, Peter P. Gaspar and John J. Root, "Kinetics, Mechanism and Hot Atom Chemistry - Present Perspectives and Future Goals."

An invited paper will be presented at the Fall 1979 American Chemical Society National Meeting, Washington, D.C., September 9-14, 1979 in the symposium entitled "Recent Developments in Biological and Chemical Research with Short-Lived Isotopes" sponsored by the Nuclear Chemistry and Technology Section: COO-1713-80, Peter P. Gaspar, "Recoil Chemistry and Mechanistic Studies with Polyvalent Atoms."

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4. 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.
5. 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.
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