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 reactions of recoiling silicon atoms and the reactions of silylene;
- b. The role of ionic reactions in the chemistry of recoiling silicon atoms;
- c. Study of silyl radical reactions by electron spin resonance spectroscopy;
- d. Production of macroscopic quantities of thermal atoms for reaction studies.

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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 the recoil reaction systems.

This summary of research accomplishments during the past year is divided into the following sections: a. Primary reactions of recoiling silicon atoms and the reactions of silylene; b. The role of ionic reactions in the chemistry of recoiling silicon atoms; c. Study of silyl radical reactions by electron spin resonance spectroscopy; d. Production of macroscopic quantities of thermal atoms for reaction studies.

Primary reactions of recoiling silicon atoms and the reactions of silylene.

In the past year the use of butadiene substrate as a probe for the primary reactions of recoiling silicon atoms has been firmly established. It was previously demonstrated that the reactions of recoiling silicon atoms produced by fast-neutron bombardment of phosphine-butadiene mixtures produces two major products, one of which was identified as [^{31}Si]-1-silacyclopent-3-ene by comparison with an authentic unlabelled sample.¹ This product has also been reported by Tang.² We have tentatively identified the second product in the past year and published our findings.³

In our previous progress report¹ we pointed out that butadiene can compete with phosphine in the primary reactions of recoiling silicon atoms,

as well as reacting with silylene. This is indicated by the observation that the silacyclopentene yield passes through a maximum with increasing butadiene concentration and is the minor product at butadiene mole fractions greater than 0.1. The yield versus composition plot for phosphine-butadiene mixtures at 1000 torr is shown below.

Since silicon atoms are believed to form silylene $^{31}\text{SiH}_2$ on reaction with phosphine, direct reaction of silicon atoms with butadiene, in competition with phosphine, should cause a decrease in the amount of $^{31}\text{SiH}_2$ formed with increasing butadiene concentration. Thus the amount of silylene addition to butadiene forming silacyclopentene should decrease. This analysis requires that the reaction of silylene with butadiene is efficient, so that the decrease in the amount of silylene which attends an increase in butadiene concentration outweighs the increase in the concentration of the trapping reagent for silylene. In an independent experiment it was demonstrated that SiH_2 from disilane pyrolysis does add efficiently to butadiene.³ The analysis above also requires that the second product not be a silylene reaction product, and this too was demonstrated in the thermally induced reaction.

The structure of the major product of reaction of silicon atoms with butadiene is of great importance, since butadiene can apparently trap silicon atoms in a single reactive collision. The structure [^{31}Si]-1-silacyclopenta-2,4-diene has been tentatively assigned on the basis of the following evidence:

- i. The molecule contains carbon, hydrogen and silicon, but not phosphorus, as indicated by its formation in silane-butadiene mixtures from silicon atoms produced by the $^{20}\text{Si}(\text{n},\gamma)^{31}\text{Si}$ nuclear transformation.
- ii. Its chromatographic behavior suggests that it is an organosilicon compound containing four carbon atoms.
- iii. An empirical formula $^{31}\text{SiC}_4\text{H}_6$ is suggested by its formation in yields nearly identical/($20 \pm 3\%$) from 1:1 PH_3 -butadiene and 1:1 PF_3 -butadiene mixtures. In the latter system there is no indication of hydrogen abstraction contributing to product formation. The other major product from PF_3 -butadiene mixtures is 1,1-difluoro- ^{31}Si -1-silacyclopent-3-ene formed in $9 \pm 3\%$ yield by fluorine abstraction.^{1,4} Thus, since we have previously shown that hydrogen abstraction from hydrocarbons by recoiling silicon atoms does not contribute significantly to product formation,⁵ it is probable that the unknown product arises from reaction of a silicon atom (or conceivably $^{31}\text{Si}^+$) with butadiene, the adduct being stabilized by rearrangement rather than by further intermolecular reaction.
- iv. Formation by direction reaction of $^{31}\text{Si} + \text{butadiene}$ is also indicated by the increase in yield accompanied by the decrease in silacyclopentene yield with increasing butadiene concentration discussed above.
- v. Silacyclopentadiene itself has not been prepared, and thus the radioactive product cannot be compared with an authentic sample. However the behavior of substituted silacyclopentadienes⁶ suggests that the unsubstituted molecule should be reasonably stable.

vi. Silicon ions Si^+ have been found in ion cyclotron resonance experiments to condense rather efficiently with butadiene: $\text{Si}^+ + \text{C}_4\text{H}_6 \rightarrow \text{SiC}_4\text{H}_6^+$.

Most alternative structures for the major product have been ruled out by direct comparison of radiochromatographic retention times of the radioactive product with authentic SiC_4H_6 , SiC_4H_8 , $\text{SiC}_4\text{H}_{10}$ and $\text{SiC}_4\text{H}_{12}$ compounds.

Among the alternative structures considered a priori most likely were:

$^{31}\text{SiH}_2$, $\text{SiH}_3\text{CH}=\text{CHCH}=\text{CH}_2$, $\text{SiH}_3\text{C}\equiv\text{CCH}=\text{CH}_2$ and $\text{SiH}_3\text{CH}=\text{CHC}\equiv\text{CH}$. All except the last of these compounds have been synthesized by the diligent effort of Mr. Hwang, the 1-silylbut-3-en-1-yne being a new compound. The synthesis of authentic compounds has been rather time consuming, but we have developed an arsenal of synthetic skills which has made the preparation of authentic compounds even when previously unknown an efficient operation.

A proposed mechanism for formation of ^{31}Si -silacyclopentadiene is given below:

While alternative structures cannot be ruled out until authentic silacyclopentadiene becomes available, they are less likely because they require more extensive rearrangement for their formation than that displayed in the mechanism above.

The formation of a product in a single reactive collision of a recoiling atom followed by intramolecular rearrangement, rather than in a complex reaction sequence, provides a powerful mechanistic tool which should greatly simplify the study of silicon atom reactions.

Since butadiene seems to react with both silicon atoms directly and with silylene, the addition of butadiene to recoiling silicon atom reaction mixtures should have a differential effect on products which result from silylene and products which arise directly from silicon atom reactions or indirectly via intermediates whose reactions with butadiene differs in efficiency from those of silylene. In the case of silylene reaction products formed in recoil silicon reaction systems, butadiene can divert precursors (^{31}Si and $^{31}\text{SiH}_2$) necessary for their formation at two stages along the reaction sequence, while for products of silicon atom reactions which do not pass through another intermediate readily scavenged by butadiene, there will only be one opportunity for butadiene to divert the necessary precursor.

We have begun very recently to reexamine reactions of recoiling silicon atoms with mono-olefins. In phosphine-ethylene mixtures silicon atoms were found in early experiments to give rise to a number of products in low yield.⁷ The reactions of silylene generated from disilane pyrolysis with ethylene are also quite complex. Cis-2-butene seems to be a quite promising substrate for mechanistic studies as its product spectrum is much less complex.

In the past year the reactions of thermally generated silylene SiH_2 , believed to be the principal intermediate in the reactions of recoiling silicon atoms in phosphine-silane mixtures, have been investigated in order to expand our understanding of the mechanisms of silylene reactions and to increase the number of known reactions. This should permit us to determine

the electronic state in which silylene is formed in recoil reactions and also the energy at which it reacts.

We have studied the stereochemistry of addition of silylene to trans-2, trans-4-hexadiene, employing disilane pyrolysis at the silylene source.⁸

While the stereochemistry of carbene addition reactions has been extensively studied in order to provide information about the electronic state of the reacting carbene,⁹ our work is the first report of the stereochemistry of a silylene addition reaction. The reactions of divalent silicon species have not previously provided information on the stereochemistry of addition since the silacyclopropane adducts are quite labile, and only ring-opened rearrangement products have been isolated.¹⁰

The addition of divalent silicon species to dienes is however known to yield cyclic products. In addition to the silacyclopentenes produced by addition to butadiene of nucleogenic ³¹SiF₂ and ³¹SiH₂ and thermally produced SiH₂, described above,²⁻⁴ the first such reaction noted was the addition of dimethylsilylene to 2,3-dimethylbutadiene:¹¹

The stereochemistry of addition of silylene to cis-2,5-dimethyl-1-silacyclopentene, that is the ratio of cis- to trans-2,5-dimethyl-1-silacyclopentene products, will

depend on the mechanistic path followed. Single-step concerted 1,4-cycloaddition should yield exclusively the cis-product. Other mechanisms predict that a mixture of stereoisomers will be formed.

We have found that almost equal quantities (product ratio 1.0 ± 0.1) of the cis and trans dimethylsilacyclopentenes are formed under conditions such that neither the starting diene nor the products undergo stereoisomerization. Thus the addition of silylene to trans,trans-hexadiene is nonstereospecific.

Two reaction mechanisms are consistent with the observed stereochemistry:

1. A diradical is formed along the reaction coordinate either as the primary adduct or from ring-opening of a vinylsilacyclopropane.

2. A vinylsilacyclopropane is formed in a concerted 1,2-addition and subsequently undergoes antarafacial and suprafacial 1,3-sigmatropic rearrangements¹² with equal facility.

A diradical mechanism seems more likely since concerted antarafacial rearrangement of an intermediate vinylsilacyclopentene involves a very

cumbersome transition state and since diradical intermediates have been demonstrated for all-carbon vinylcyclopropane-to-cyclopentene rearrangements.¹³

Addition of silylene to cyclopentadiene has also been investigated. The major product has been identified as 1-silacyclohexa-2,4-diene.

This product can also be rationalized by a mechanism involving a diradical intermediate:

A similar product has been obtained from copyrolysis of hexachlorodisilane and butadiene by Russian workers.¹⁴

Combination of the mechanism suggested above with that of p. 4 for the formation of silacyclopentadiene from the reaction of recoiling silicon atoms with butadiene suggests that the reaction of recoiling silicon atoms

with cyclopentadiene might lead to the formation of silabenzene:

While C=Si π -bonds have been widely shunned in mechanistic arguments because of the belief that they are very weak due to poor 2p-3p π -overlap, recently C=Si, Si=Si and Ge=C and Si=O bonds have been experimentally demonstrated.¹⁵

Reactions of recoiling silicon atoms in phosphine-butadiene mixtures have been examined, but preliminary experiments have not produced any volatile radioactive products. Since all other dienes have given considerable yields of radioactive products, we believe that an unstable product was formed which was sufficiently reactive to form high molecular weight

products upon further reaction with cyclopentadiene or phosphine. We are seeking to confirm this suggestion by adding suitable secondary reactants to convert silabenzene into a stable product, e.g.:

The experiments in this area have been carried out by Mr. Rong-juh Hwang.

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

Nearly three years ago we began to examine the possibility that silicon ions may play an important role in the chemistry of recoiling silicon atoms.^{1,16} We were prompted to pursue this avenue of investigation by consideration of the implications of the extraordinarily low ionization potential of atomic silicon, 8.14 V,¹⁷ and by reconsideration of the application of the resonance rule¹⁸ to the problem of deciding whether recoiling silicon atoms enter the energy zone of hot atom reactions as neutral atoms or as positive ions. Since the ionization potential of silicon atoms is much lower than that of the medium in which they are formed, there is considerable opportunity for recoiling $^{31}\text{Si}^+$ ions to reach energies sufficiently low for bond-making processes to occur. This is emphasized by calculations based on the resonance rule.⁷ These indicate that the cross-sections for neutralization of Si^+ ions reach maxima at energies only one power of ten (eV) below those for ionization. This should be compared with the situation for carbon for which resonance rule calculations indicate that maxima for neutralization cross-sections occur three powers of ten lower in energy than those for ionization.¹⁹ Thus recoiling silicon atoms cascading from very high initial energies should have finite probability for reaching energies at which they

can undergo bond-making processes as ions. Also any recoiling silicon atom which emerges as an ion from the molecule in which the parent nuclide was incorporated by recoil from a low-energy nuclear reaction such as $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ should undergo bond-forming reactions as ions, if low-energy ion-molecule reaction channels exist, since neutralization cross-sections for low energy silicon ions in collisions with molecules of higher ionization potential will be small.

Therefore we began a series of experiments designed to answer the questions: 1. Can a sequence of ion-molecule reactions initiated by an ionic silicon recoil species $^{31}\text{Si}^+$ give rise to the observed products from silicon atoms recoiling in simple systems such as pure silane and phosphine-silane mixtures? 2. Do the reactions of recoiling silicon ions play an important role in hot atom reaction systems?

The first question has been answered affirmatively by studying the reactions of Si^+ , SiH^+ , SiH_2^+ and SiH_3^+ by ion cyclotron resonance spectroscopy. Although previous investigations of ion-molecule reactions in silane by high pressure mass spectroscopy had indicated that only SiH_2^+ is reactive toward silane,²⁰ we were convinced on the basis of the thermochemistry of silicon ions²¹ that Si^+ , SiH^+ and SiH_3^+ should all undergo reaction. Ion cyclotron resonance (icr) spectroscopy did indeed reveal a rich chemistry for all the ions above,²² and the new reactions which we reported have subsequently been confirmed by high pressure and tandem mass spectrometric experiments.²³

The rate constants which we obtained from icr experiments on exothermic reactions of silicon-containing ions,²² and the kinetic energy dependence of endothermic reaction rates,²⁴ are useful for the understanding of the mechanisms of the observed ion-molecule reactions and the kinematics of fragmen-

tation of excited intermediate ions. Isotopic labelling experiments have been employed to demonstrate the formation of long-lived complexes in ion-molecule reactions in silane-methane mixtures.²⁵⁻²⁷

By far the most important result which has emerged from our ion-molecule reaction studies in so far as its furthering our understanding of silicon atom recoil chemistry is that the reactions of $^{31}\text{Si}^+$ ions in silane would be expected to produce trisilane incorporating the recoiling atom as a stable end product, but not silane and disilane.²⁸

Observation of the following efficient reactions at the low pressures (10^{-6} - 10^{-5} torr) of the icr experiment

and the failure to observe the following hydride-transfer reaction

suggested that at the high pressures present in recoil experiments silicon ions in the presence of silane should undergo the following reaction sequence in pronounced preference over other modes of reaction.²⁸

The condensation reactions $\text{Si}^+ + \text{SiH}_4 \longrightarrow \text{Si}_2\text{H}_4^+$ and $\text{Si}_2\text{H}_4^+ + \text{SiH}_4 \longrightarrow \text{Si}_3\text{H}_8^+$ have been observed directly in high pressure mass spectrometric experiments by Lampe and coworkers.²³

From our icr experiments a prediction emerged: If silicon ions are

involved in the chemistry of recoiling silicon atoms in phosphine-silane mixtures, they will be incorporated in the trisilane product rather than in the silane and disilane also observed. (In 1:1 phosphine-silane mixtures at 1000 torr absolute yields are: $^{31}\text{SiH}_4$ $13 \pm 2\%$, $^{31}\text{SiSiH}_6$ $48 \pm 5\%$, and $^{31}\text{SiSi}_2\text{H}_8$ $7 \pm 2\%$).

The second question, do the reaction of recoiling ions play an important role in hot atom reaction systems, has been examined by employing aliphatic amines as "ion scavengers." Triethylamine and trimethylamine are attractive reagents because their ionization potentials are even lower than that of atomic silicon (ionization potentials: Si 8.12, Et_3N 7.50, Me_3N 7.82 V),¹⁷ suggesting that charge exchange between these amines and Si^+ might be rapid. This was shown to be the case for Et_3N by directly measuring the rate of electron exchange by icr spectroscopy.²⁸ Therefore the addition of Et_3N and Me_3N to phosphine-silane hot atom reaction mixtures could be expected to cause rapid neutralization of any $^{31}\text{Si}^+$ ions present. This would cause a change in the product spectrum if $^{31}\text{Si}^+$ and $^{31}\text{Si}(3\text{P})$ (the product of charge exchange) differed in their reactivity. It is expected that silicon ions and ground state silicon atoms differ in their reactions with silane, but this has not yet been verified. If however neutral silicon atoms can also give rise to trisilane by the path shown below,

a reaction sequence supported by the work of Skell²⁹ and Ring,³⁰ then simple neutralization might not manifest itself in a change in the product spectrum.

Preliminary experiments²⁸ have indicated that the presence of Et_3N and Me_3N do cause significant decrease in the trisilane product yield without affecting the silane and disilane yields, just as is expected if $^{31}\text{Si}^+$ is a

necessary intermediate in trisilane formation and neutralization of $^{31}\text{Si}^+$ reduces the probability for trisilane formation. Preliminary experiments also indicated that other alkylamines and ammonia itself, all with ionization potentials higher than that of silicon atoms, cause a decrease in the trisilane yield. This observation was explained by pointing out that $^{31}\text{Si}^+$ ions with excess kinetic energy might undergo endothermic charge exchange, and also that Si^+ might react with alkyl amines and ammonia in ion-molecule reactions other than charge exchange. One such reaction was reported in the previous progress report.¹

This background sets the stage for a report of the past years' experiments in this area.

In the past year a large number of hot-atom experiments were carried out in which we studied the effect of various added amines on the yields of silane, disilane and trisilane from fast-neutron irradiations of phosphine-silane mixtures.

A quantitative model has been developed to relate the reduction in trisilane yield in the presence of amine to such factors as the relative efficiency of the reactions of intermediates with silane and amine, the number of steps in the reaction sequence which converts a silicon ion to trisilane, and the mole fraction of amine present. This model is an idealized recoil reaction system based on the following assumptions:

1. Non-ionic reaction channels are not affected by the presence of amines and are therefore ignored.
2. The role of phosphine is the same in the presence and absence of amine and is therefore ignored.
3. Every ion-molecule encounter is reactive (this is a mathematical simplification which, while unrealistic, is equivalent to a scaling factor).
4. The macroscopic components of the reaction system remain in constant concentration during

a recoil experiment. 5. Reactions of $^{31}\text{Si}^+$ ions with silane initiate a sequence of reactions which can be terminated at any stage before the final product is formed by a reaction of $^{31}\text{Si}^+$ or some subsequent ionic intermediate with an amine molecule. The minimum number of steps in the reaction sequence is given by the reaction scheme presented on p. 12.

From the model described above an expression can be derived for the reduction in the trisilane yield caused by the presence of mole fraction A of amine:

$$[^{31}\text{SiSi}_2\text{H}_8]_A / [^{31}\text{SiSi}_2\text{H}_8]_0 = (1 - A\bar{E})^{\bar{n}}$$

in which $\bar{E}$ is the average ratio of rate constants for reactions of all intermediate ions with amine versus reaction with silane, and $\bar{n}$ is the average number of steps in all reaction sequences which operate simultaneously to convert $^{31}\text{Si}^+$ ions in silane to trisilane.

Our model is equivalent to an extension to multi-step reactions of the statistical model for recoiling iodine ion reactions in methane developed by Rack and Gordus.³¹ A related model was applied by Loberg and Welch.³²

The expression derived from our model and given above relates trisilane yield to two parameters $\bar{E}$ and $\bar{n}$. By assumption $\bar{n}$ the number of steps in the reaction sequence which converts $^{31}\text{Si}^+$ to trisilane is not affected by the identity of the amine used in a given experiment as an ion scavenger. The relative efficiency of silane and amine in capturing the reactive ionic intermediates $\bar{E}$ will of course depend on the specific amine employed. Therefore, if this model is reasonable, it should be possible to fit trisilane yield versus amine concentration curves for various amines to a single value of $\bar{n}$ and a set of $\bar{E}$ values representing the relative ion-scavenging efficiency of each amine. A start has been made at the use of the theory of ion-molecule reaction rates to calculate rate constants for various silicon ionic

intermediates in their reactions with silane and various amines, thus generating predicted $\bar{E}$ values. $\bar{n}$ can also be predicted from such reaction schemes as shown on p. 12. The merit of our model and the expression derived from it will lie in the demonstration that the effects of amines as ion scavengers is consistent with what is known about the kinds of reactions sequences which can convert Si^+ ions into trisilane and about the reactivity of amines toward silicon ions.

To definitely test the general idea that ion-molecule reactions are important in the chemistry of recoiling silicon atoms and to test the model outlined above, accurate trisilane yield versus amine concentration data are needed and are being collected. Considerable difficulty has been encountered in obtaining reproducible yield curves due to the circumstance that the critical product trisilane is more vulnerable to attack by impurities and to radiation damage than are any of the macroscopic components of the reaction mixtures. Recently small amounts of trisilane have been employed as internal carrier present throughout neutron irradiation and subsequent radiochromatographic analysis. Reproducible data are now being obtained and will allow us to assess quantitatively the role of silicon ions in recoil atom chemistry.

As a further probe for the importance of $^{31}\text{Si}^+$ ions in the recoil system a special reaction cell was built in which the reactions of silicon atoms recoiling in phosphine-silane mixtures could be carried out in a strong electric field, variable from 0 to 3000 volts/cm. A decrease in trisilane yield relative to silane and disilane with increasing electric field strength was observed, the relative yield of trisilane decreasing by ca. 25%. Since we are limited to rather high pressures (ca. 10 torr of 1:1 $\text{PH}_3\text{-SiH}_4$) in order to obtain sufficient radioactivity for analysis, the mean free paths

of silicon ions are very small, and thus any ions formed gain very little energy by acceleration due to the field before reaction. Therefore the effect of the field in our system is probably only to remove any ions formed near the anode. Nevertheless it seems that the trisilane yield is reduced by the action of the electric field, a result consistent with an important role for ions as precursors to the trisilane product. This experiment requires careful controls as does the amine scavenger experiment to insure that the decrease in trisilane yield is due to removal of the necessary precursor rather than to destruction of the trisilane product after formation.

The reactions of Si^+ , SiH^+ , SiH_2^+ and SiH_3^+ with Et_3N , Me_3N , Me_2NH , MeNH_2 and NH_3 have been carefully examined by icr spectroscopy in order to increase our understanding of their action as ion scavengers in recoil reaction mixtures. Interestingly Et_3N undergoes charge exchange with the various SiH_n^+ ions ($n = 0, 1, 2, 3$) as the sole detectable ion-molecule reaction. The methylamines undergo a variety of ion-molecule reactions in addition to charge exchange. These reactions are given in tabular form indicating the reaction products and the sign of the change in rate constant with increase in reactant ion energy dk/dE in Table I. The reactions of such important intermediate ions as Si_2H_2^+ and Si_2H_4^+ ions with the methylamines and ammonia were also examined and the results given in Table II. The wide variety of exothermic and therefore probably rapid reactions between Si^+ and all methylamines studied (an exothermic reaction is indicated by negative dk/dE , but charge transfer reactions with positive dk/dE can also be exothermic) indicates that these amines with ionization potentials above that of silicon atoms could nevertheless act as efficient silicon ion scavengers.

Since phosphine is present as the molecule containing the parent nuclide for recoiling silicon atoms in most of our hot atom experiments, it too is a

TABLE I

	NH ₃	δk/δE	CH ₃ NH ₂	δk/δE	(CH ₃) ₂ NH	δk/δE	(CH ₃) ₃ N	δk/δE
Si ⁺	SiNH ₂ ⁺ + H	-	MeNSiH ₂ ⁺ + H	-	Me ₂ NSi ⁺ + H	-	Me ₂ NSi ⁺ + CH ₃	-
			SiNH ₂ ⁺ + CH ₃		Me ₂ N ⁺ + SiH	+	Me ₃ N ⁺ + Si	+
							Me ₂ N ⁺ + Si + CH ₃	+
SiH ⁺	SiNH ₂ ⁺ + H ₂	-	MeNSiH ₂ ⁺ + H	-	Me ₂ NSi ⁺ + H ₂	-	Me ₂ NSi ⁺ + CH ₄	-
	SiNH ₃ ⁺ + H	-	MeNSiH ₃ ⁺	-	Me ₂ NSiH ⁺ + H	-	Me ₃ NSiH ⁺	-
			SiNH ₃ ⁺ + CH ₃	-			Me ₂ NSiCH ₂ ⁺ + H ₂	-
			SiCH ₃ ⁺ + NH ₃	-			Me ₃ N ⁺ + SiH	+
	SiNH ₃ ⁺ + H ₂	-	MeNSiH ₂ ⁺ + H ₂	- +	Me ₂ NSi ⁺ + H ₂ + H	-	Me ₃ NSiH ⁺ + H	-
	SiNH ₄ ⁺ + H	-	MeNSiH ₃ ⁺ + H	-	Me ₂ NSiH ⁺ + H ₂	-	Me ₃ NSiH ₂ ⁺	-
	NH ₄ ⁺ + HSi	-	MeNSiH ₄ ⁺	-	Me ₂ NSiH ₂ ⁺ + H	-	Me ₂ NSiH ₂ + CH ₃	-
SiH ₂ ⁺			MeNSiH ⁺ + H ₂ + H	-	Me ₂ NSiH ₃ ⁺	-	Me ₂ NSi ⁺ + CH ₃ + H ₂	-
			SiNH ₄ ⁺ + CH ₃	-	Me ₂ N ⁺ + SiH ₃	+	MeNSiH ₂ ⁺ + C ₂ H ₆	+ -
			MeSiH ₃ ⁺ + NH		Me ₂ NH ⁺ + SiH ₂	+	Me ₂ NCH ₂ ⁺ + SiH ₃	+
			MeSiH ⁺ + NH ₃		Me ₂ NH ₂ ⁺ + SiH	+	Me ₃ N ⁺ + SiH ₂	+
			MeNH ₂ ⁺ + SiH ₂	+				

TABLE I (cont'd)

	NH ₃	δk/δE	CH ₃ NH ₂	δk/δE	(CH ₃) ₂ NH	δk/δE	(CH ₃) ₃ N	δk/δE
SiH ₃ ⁺	SiNH ₄ ⁺ + H ₂	-	MeNSi ⁺ + 2H ₂ + H	+	Me ₂ NSi ⁺ + 2H ₂	-	Me ₃ NSiH ⁺ + H ₂	-
	SiNH ₅ ⁺ + H	-	MeNSiH ₂ ⁺ + H ₂ + H	+ -	Me ₂ NSiH ₂ ⁺ + H ₂	-	Me ₃ NSiH ₂ ⁺ + H	-
			MeNSiH ₃ ⁺ + H ₂	-	Me ₂ NSiH ₃ ⁺ + H	-	Me ₃ NSiH ₃ ⁺	-
			MeNSiH ₄ ⁺ + H	-	MeN ⁺ + SiH ₄	-	Me ₂ NSiH ₂ ⁺ + CH ₃ + H +	
			MeNH ₃ ⁺ + SiH ₂	-	Me ₂ NH ⁺ + SiH ₃	+	Me ₂ NSiH ₃ ⁺ + CH ₃	-
					Me ₂ NH ₂ ⁺ + SiH ₂	+	MeNSiH ⁺ + C ₂ H ₆ + H ₂	-
							MeNSiH ₂ ⁺ + C ₂ H ₆ + H	+
							MeNSiH ₃ ⁺ + C ₂ H ₆	+
							Me ₂ NCH ₂ ⁺ + SiH ₄	-
							Me ₃ N ⁺ + SiH ₃	+
						Me ₃ NH ⁺ + SiH ₂	+	

TABLE II

NH_3	$\delta k/\delta E$	CH_3NH_2	$\delta k/\delta E$	$(\text{CH}_3)_2\text{NH}$	$\delta k/\delta E$	$(\text{CH}_3)_3\text{N}$	$\delta k/\delta E$
Si_2H_2^+		$\text{MeNSiH}^+ + \text{SiH}_3 + -$		$\text{Me}_2\text{NSi}^+ + \text{SiH}_3$	?	$\text{CH}_2\text{NSi}^+ + \text{C}_2\text{H}_6 + \text{SiH}_3$	?
$\text{SiNH}_3^+ + \text{SiH}_4$	-	$\text{MeNSiH}_5^+ + \text{SiH} + -$		$\text{Me}_2\text{NSiH}^+ + \text{SiH}_4 + -$		$\text{Me}_2\text{NSi}^+ + \text{CH}_3 + \text{SiH}_4 + -$	
$\text{SiNH}_6^+ + \text{SiH}$	-	$\text{MeNSiH}_2^+ + \text{SiH}_4 -$		$\text{Me}_2\text{NSiH}_2^+ + \text{SiH}_3 + -$		$\text{Me}_2\text{NSiCH}_2^+ + \text{SiH}_4 + \text{H} -$	
Si_2H_4^+				$\text{Me}_2\text{NSiH}_3^+ + \text{SiH}_2 + -$		$\text{Me}_3\text{NSiH} + \text{SiH}_3$	+ -
				$\text{Me}_2\text{NSiH}_4^+ + \text{SiH} + -$		$\text{Me}_3\text{NSiH}_2 + \text{SiH}_2$	+ -

potential silicon ion scavenger. Therefore we studied reactions of SiH_n^+ ions ($n = 0, 1, 2, 3$) with PH_3 by icr spectroscopy. The results are given in Table III. It can be seen that all silicon ions except SiH^+ react with phosphine. Prediction of the relative efficiency of reaction of phosphine versus silane toward Si^+ indicates that phosphine should be a potent ion scavenger. Ideally then the effect of other ion scavengers such as amines would be examined in the presence of a phosphorus compound less prone to acting as an ion scavenger.

In the course of studying the reactions of Si^+ , SiH^+ , SiH_2^+ and SiH_3^+ with ammonia we found that observable quantities of the interesting ion SiH_5^+ could be obtained in the ion cyclotron resonance spectrometer from the reaction first observed at higher pressures by Lampe.³³ We were able to determine the rate constant.

We also found that proton transfer to silane from methanim ion is an efficient exothermic reaction:

These rate constants were measured for the first time.

In our experiments³⁴ the first reported ion-molecule reaction of SiH_5^+ was observed, and a remarkable specificity was noted when isotopically labelled SiD_4H^+ (from $\text{NH}_2^+ + \text{SiD}_4$) was employed in the reaction studies.

TABLE III

Silicon ion	Reaction with PH_3	k_{rel}
Si^+	$\text{SiPH}^+ + \text{H}_2$	0.02
SiH^+	----	----
SiH_2^+	$\text{PH}_4^+ + \text{SiH}$	0.18
	$\text{SiPH}_2^+ + \text{H}_2 + \text{H}$	0.01
	$\text{SiPH}_3^+ + \text{H}_2$	0.03
	$\text{SiPH}_4^+ + \text{H}$	0.03
SiH_3^+	$\text{PH}_4^+ + \text{SiH}_2$	0.17
	$\text{SiPH}_4^+ + \text{H}_2$	0.08
	$\text{SiPH}_5^+ + \text{H}$	0.003
	SiPH_6^+	0.001

The surprising result that the condensation of SiD_4H^+ and NH_3 proceeds with nearly exclusive loss of HD (rather than H_2 or D_2) has interesting mechanistic and structural implications. A direct reaction without an intermediate such as direct displacement is suggested. The structural inference is that the H atom in SiD_4H^+ is chemically distinguishable from the D atoms. For an isotope effect to explain this preference for HD loss a $k_{\text{H}}/k_{\text{D}}$ ratio greater than 15 would be required. We prefer instead to conclude that the H atom is structurally distinct and chemically labile in SiD_4H^+ . Based on our work, described below, the most likely structure of SiD_4H^+ is of C_s symmetry, a structure not even considered previously in calculations on the energy of SiH_5^+ which considered as possible structures only molecular symmetries C_{4v} and D_{3h} .³⁵ The C_s symmetry is however that assigned to the ground state of CH_5^+ on the basis of calculations and our experimental evidence (see below).

If SiD_4H^+ has C_s symmetry with the H (which was transferred to SiD_4) taking part in the two electron three-center bond, then direct displacement is an attractive description of the condensation reaction with ammonia:

This picture contains more detail than the icr experiments strictly warrant, since the structure of the $\text{SiNH}_3\text{D}_3^+$ ion is not established from our experiments. It is however in accord with a direct displacement on SiD_4H^+ in which exclusive loss of HD occurs, as was observed. Strictly speaking, our evidence for the structure of SiD_4H^+ is that the H^+ added to SiD_4 is among the two most weakly bound hydrons in the SiD_4H^+ ion. D_{3h} and C_{3v} structures also fulfill this criterion:

The C_{3v} structure is unlikely because its energy is probably much higher than that of other structures. The D_{3h} model requires exclusive loss of the axial H and D, which is most unlikely.

The surprising result that the hydrons of SiD_4H^+ are structurally distinguishable led us to examine hydron transfer to methane and from the methanium ion CH_5^+ and also collision-induced dissociation of CH_5^+ .

While CH_5^+ has been one of the most widely studied ions (other than H^+) since it was first observed in 1952,³⁶ it has previously been assumed in all

previous studies that the five hydrogens are chemically equivalent on the experimental time scale, i.e. either geometrically equivalent or if not, interconverting rapidly on the time scale of chemical reactions.

The geometrical nonequivalence of the hydrogens has been established beyond reasonable doubt by the calculations of Gamba, Morosi and Simonetta,³⁷ of Ehrenson,³⁸ and of Dyczmons, Staemmler and Kutzelnigg.²⁹ These workers all concluded that ground state CH_5^+ possesses C_s symmetry. These calculations predict that two of the hydrogens participate with the carbon in a three-center two-electron bond while the other three C-H bonds are normal, nearly tetrahedral, bonds. The results of the most accurate calculation³⁹ are shown below:

If one accepts the theoretical prediction that the hydrogens of CH_5^+ are structurally distinguishable, falling into two groups consisting of two and three hydrogens respectively, there remains the question of structural integrity - how difficult is it for the hydrogens to exchange positions? Ehrenson has addressed this problem and has calculated a 0.1 eV barrier to interconversion of the two kinds of hydrogens by the process shown below.

We have found experimentally in icr reaction studies that the hydrogens of methanium ion are indeed chemically distinguishable, and do not scramble rapidly on the millisecond time scale of icr spectroscopy.⁴⁰

We have made CH_4D^+ and CD_4H^+ by the following well-known ion-molecule reactions:

and studied the hydron transfer reactions from these isotopically labelled methanium ions to such hydron acceptors as olefins, alkynes, nitriles, ethers, epoxides, silane and cyclopropane. Collision-induced dissociation was also studied.

A large preference for D^+ versus H^+ loss from CH_4D^+ and for H^+ versus D^+ loss from CD_4H^+ was observed.⁴⁰ It was deduced that there is roughly a 50% probability for loss of D^+ from CH_4D^+ and for loss of H^+ from CD_4H^+ .

This result supports the C_s model for the structure of the methanium ion since hydron transfer to methane should incorporate the added hydron

into the three-center bond and make it structurally equivalent with one other hydron in methanium. Therefore loss of one hydron from the three-center bond should eliminate the added hydron 50% of the time.

According to this model, elimination of a hydrogen molecule as in collision-induced dissociation:

should eliminate both hydrons held in the three-center bond and thus always lead to loss of the hydron transferred to methane. Experimentally we have observed predominant loss of HD (over H_2 and D_2 from both CH_4D^+ and CD_4H^+).

Furthermore when the internal energy of the methanium ion is raised by employing a more exothermic hydron transfer reaction to produce the methanium ion ($\text{H}_3^+ + \text{CH}_4 \longrightarrow \text{CH}_5^+ + \text{H}_2$) HD is no longer lost preferentially from CH_4D^+ and CD_4H^+ upon collision-induced dissociation, indicating that hydrogen scrambling by intramolecular rearrangement prior to reaction has occurred. This is reasonable since the rate of scrambling should increase with increase in internal energy.

Thus under the low energy conditions of the icr experiment where the reactions of thermal energy ions are studied and where the total energy

of the methanium ion is less than 0.5 eV and the internal energy less than 0.2 eV, the hydrogens of the methanium ion are chemically distinguishable. The relative probabilities for loss of H^+ versus D^+ , and for loss of HD versus H_2 and D_2 , from CD_4H^+ and CH_4D^+ are in accord with a C_s structure for the methanium ion.

As indicated in our paper, these results are somewhat complicated by the difficulty of accurately assessing isotope effects and by the formation of labelled methanium ions by a hydrogen atom transfer in addition to the proton transfer mechanism.

We have also begun the investigation of doubly charged ions which may play a role in the chemistry of recoiling silicon and germanium ions. GeH_2^{++} has been observed by ion cyclotron resonance spectroscopy. Since monopositive ions GeH_n^+ ($n = 0, 1, 2, 3$) vastly outnumber the dipositive ions, the experimental problem is to sort out the reactions of the dipositive ions from the monopositive ions reactions. This will require isotopically enriched germanium.

The experiments of this section were carried out by Dr. Sefcik and Mr. Mizes.

c. Study of silyl radical reactions by electron spin resonance spectroscopy

Having previously studied the dimerization of silyl radicals⁴¹ and the addition of silyl radicals to olefins⁴² we turned our attention this past year to a new reagent for silyl radical production - diphenylmethylene.

While photolysis of t-butyl peroxide in the presence of silanes has been a successful method for the formation of unsubstituted and alkyl substituted silyl radicals,

it fails entirely in the generation of detectable amounts of silyl radicals with aryl substituents.

Assuming that this failure to observe arylsilyl radicals when solutions of arylsilanes in t-butyl peroxide are irradiated with ultraviolet light is due to an internal filtering effect by the aryl groups, we decided to use a reagent which is activated by visible light to abstract hydrogen atoms from arylsilanes. Purple diphenyldiazomethane seemed an ideal choice since diphenylmethylene is known to abstract hydrogen atoms from carbon-hydrogen bonds.

Therefore solutions of diphenyldiazomethane in aryl (and alkyl) silanes were irradiated with visible light in situ in the microwave cavity of the esr spectrometer. While strong esr signals were obtained in all cases, large nitrogen hyperfine splittings indicated that the observed radicals were not the desired silicon-centered arylsilyl radicals. It was determined that the esr signals were due to a new class of nitrogen-centered radical, the iminamino radicals $\phi_2\text{C=N-N-SiR}_3$.⁴³ These are long-sought nitrogen analogs of the well-studied iminoxy radicals $\text{R}_2\text{C=N-O}\cdot$.

The finding of silylhydrazones of benzophenone among the reaction products, as well as the observation of the iminamino radicals, suggested the following reaction scheme, illustrated for $\phi_2\text{SiH}_2$:

Among the isolated products from HSiMe_3 were $\text{Me}_3\text{SiSiMe}_3$, $\text{Me}_3\text{SiCH}\phi_2$ and $\phi_2\text{CHCH}\phi_2$. While hexamethyldisilane must result from radical dimerization, the latter products may arise from attack of radicals at the other end of the diazo compound.

While it appears that diphenylmethylene does successfully abstract hydrogen atoms from arylsilanes, its precursor diphenyldiazomethane is too efficient as a radical trap to permit the observation of the arylsilyl radicals formed on the 0.1 millisecond time scale of our experiment.

In the past we have been limited in the time resolution of our flash photolysis esr kinetic studies to ca. 0.1 msec by the 10 kilocycle magnetic field modulation employed for signal stabilization and signal-to-noise enhancement. In contrast our xenon flashlamp has a rise and fall time of ca. 10 microseconds.

We have now completed assembling a flash photolysis esr apparatus capable of time resolution down to 100 nanoseconds. In collaboration with Professor S. I. Weissman we are adopting Fessendon's method for automatic frequency control in which the microwave signal reflected from the esr cavity is

sampled and its phase compared with a reference signal from the klystron.⁴⁴ Thus field modulation is being abandoned in order to enhance time resolution by ca. 10^3 . This should permit the reactive short-lived arylsilyl radicals to be observed as well as facilitating attempts to prepare neutral SiH_5 and GeH_5 by the addition of hydrogen atoms to silane and german at low temperatures.

The experiments of this section have been carried out by Dr. Choo and Mr. Ho (a student whose work is principally in the area of carbene chemistry) and Dr. Sefcik.

d. Production of macroscopic quantities of thermal atoms for reaction studies

We have already presented in this progress report evidence that the reactions of recoiling silicon atoms with butadiene produce the unknown compound silacyclopentadiene, and we have speculated about the formation of silabenzene from silicon atoms and cyclopentadiene. Since silacyclopentadiene and silabenzene are inaccessible from conventional synthetic procedures, it is important to examine the reactions of macroscopic quantities of silicon atoms with dienes and other substrates. This will provide bulk quantities, i.e. milligrams to grams of reaction products which can be characterized by spectroscopic and chemical methods, and, if their chromatographic behavior proves them to be identical to the recoil reaction products, will aid in their identification. Comparison of the products from recoil atom reaction systems with those from thermal silicon (and germanium) atoms can assist in the sorting out hot from thermal recoil atom reaction products and also help discriminate products of neutral atom reactions from products of ionic reactions.

To this end we have begun studying the reactions of thermally evaporated germanium atoms and will shortly begin studying silicon atoms.

Very little has been published about the reactions of thermally evaporated silicon and germanium atoms.⁴⁵ Skell and Owen have reported the condensation with trimethylsilane of silicon atoms evaporated by resistive heating of silicon at 1400° produced as sole product 1,1,1,3,3,3-hexamethyltrisilane:²⁹

Similar reactions were reported by these workers for silicon atoms obtained by electron bombardment and mono- di- and trimethylsilane and disilane as reaction substrates. It should be recalled that recoiling silicon atoms reacting with trimethylsilane produce 1,1,1-trimethyldisilane $\text{Me}_3\text{Si}^{31}\text{SiH}_3$ in addition to smaller quantities of $\text{Me}_3\text{Si}^{31}\text{SiH}_2\text{SiMe}_3$.¹ The mechanism of this reaction is still under investigation.

Kirk and Timms have reported the following reaction to proceed in 1% yield with silicon evaporated by electron bombardment.⁴⁶

We have constructed a high temperature evaporation source, a microcrucible consisting of an alumina-coated molybdenum wire spiral with a capacity of ca. 1 ml. Resistive heating of this crucible to 1500° has allowed the evaporation of germanium. Cocondensation of the germanium vapor with trimethylsilane in the apparatus schematically represented below led to the formation of bis-trimethylsilylgermane $\text{Me}_3\text{SiGeH}_2\text{SiMe}_3$, presumable via trimethylsilylgermylene intermediate:

This reaction is not surprising in light of our finding $\text{SiH}_3^{75}\text{GeH}_2\text{SiH}_3$ among the products from germanium atoms recoiling in germane-silane mixtures.⁴⁷ It is of interest however that thermal germanium atoms and the divalent germanium intermediate undergo facile silicon-hydrogen insertion.

Thermal evaporation of silicon from alumina crucibles is hindered by the rapid attack of the crucible by silicon at elevated temperatures. Other crucible materials are being tested.

It is desirable to employ both resistive heating and electron beam bombardment to evaporate silicon and germanium since under electron bombardment ions may be produced as well as neutral atoms. Thus comparison of the two sources of silicon and germanium atoms will be of interest. In the only such comparison reported to date, Skell and Owen found that the yield of hexamethyltrisilane from silicon atoms and trimethylsilane was higher (27%) when the silicon was resistively heated than when an electron beam was used to evaporate the silicon (yield 14%).²⁹

The experiments of this section were carried out by Mr. Robert T. Conlin with the assistance of Dr. Sefcik.

PERSONNEL

In the past year Dr. Michael Sefcik has contributed enormously to our research program carrying out experiments in ion-cyclotron resonance spectroscopy, flash-photolysis esr studies of silicon atom reactions, and silicon atom recoil studies. He has just been hired as a research chemist in the Central Research Department of Monsanto in Saint Louis, and we look forward to continued fruitful collaboration. This opportunity for Dr. Sefcik came suddenly, and we are corresponding with several candidates as replacements for him. Two important papers coauthored by Dr. Sefcik are in the press, and another is nearing completion.

Since June 1 Dr. Maurizio Speranza, a coworker of Professor Fulvio Cacace and Dr. Angelo Guarino in the Laboratorio di Chimica Nucleare del C. N. R., Rome, Italy has been working in our laboratory. He has come to Saint Louis for six months to apply our methods for the study of ion-molecule reactions of intermediates in recoil reaction systems to the reactions of vigorous protonating agents such as CH_5^+ and H_3^+ with substituted benzenes. His salary and travel expenses are being paid by the C. N. R., with a supplement from Washington University. There is no charge being made to AEC funds although Dr. Speranza is investigating some reactions which pertain to our interests.

Mr. Rong-juh Hwang, a graduate student beginning his fourth year of graduate study and third year working on this project continues to contribute to our knowledge of the reaction mechanisms for recoiling silicon atoms. Barry Mizes, about to start his junior year of undergraduate work has worked 18 months in our group and now carries out research independently on the recoil studies in the phosphine-trimethylsilane and trimethylphosphine-trimethylsilane systems and on the amines as ion scavengers in the phosphine-silane system.

Two other graduate students, not paid by AEC funds, have contributed to the research effort this past year. Both Robert T. Conlin and Chi-Tang Ho have been working on carbene chemistry. Mr. Ho became interested in the reactions of diphenylmethylene with silanes as sources of silyl radicals and collaborated with Mr. (now Dr.) Ho in experiments described in this report. Mr. Conlin has constructed apparatus for the evaporation of silicon and germanium and studied the reactions of thermally evaporated germanium atoms with trimethylsilane.

The fruitful collaboration over the past three years with Dr. Jay Henis of the Central Research Department of the Monsanto Company, St. Louis, should also be acknowledged. His expertise in the study of ion-molecule reactions by ion cyclotron resonance spectroscopy and our interest in silicon atom recoil atom chemistry have been combined in a fruitful series of investigations of silicon ion reactions which has increased our understanding of the recoil systems as well as our knowledge of the mechanisms and kinematics of ion-molecule reactions.

PUBLICATIONS

Three papers have appeared in the last twelve months:

1. COO-1713-33 "Reactions of Recoiling Germanium Atoms in Germane, Digermane and Germane-Silane Mixtures" by Peter P. Gaspar and John J. Frost. J. Amer. Chem. Soc., 95, 6567 (1973).
2. COO-1713-40 "Reactions of Recoiling Silicon Atoms with Phosphine and Butadiene, and the Addition of Silylene to Butadiene" by Peter P. Gaspar, Rong-Juh Hwang and William C. Eckelman, J. Chem. Soc., Chem. Comm., 242 (1974).
3. COO-1713-41 "Addition of Trimethylsilyl Radical to Ethylene. A Flash Photolysis-Electron Spin Resonance Kinetic Study" by Kwang Yul Choo and Peter P. Gaspar, J. Amer. Chem. Soc., 96, 1284 (1974).

Five 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-1713-42 "Selective Hydrogen Elimination from Ion-Molecule Reaction Intermediates in Silane-Methane Mixtures" by J.M.S. Henis, G.W. Stewart and P.P. Gaspar, J. Chem. Phys., in the press.
3. COO-1713-46 "Stereochemistry of a Silylene Addition Reaction" by Peter P. Gaspar and Rong-Juh Hwang, J. Amer. Chem. Soc., in the press.
4. COO-1713-47 "The Methanium Ions, CH_5^+ . Evidence for the Structure of a Non-classical Ion from Reaction Studies by Ion Cyclotron Resonance Spectroscopy" by Michael D. Sefcik, Jay M.S. Henis, and Peter P. Gaspar, J. Chem. Phys., in the press.

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., in the press.

One additional paper has been submitted for publication:

1. 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, submitted for publication to J. Amer. Chem. Soc.

Another technical report was the invited paper given by the principal investigator at the Seventh International Hot Atom Symposium, Juelich, Germany, September 11, 1973: COO-1713-44 "The Hot Atom Chemistry of Polyvalent Atoms".

STATEMENT OF EFFORT

The principal investigator was in Europe for four months last fall and winter from September 7, 1973 to January 9, 1974. The first month was spent in Germany, Switzerland and Holland, attending and delivering an invited paper plus a contributed paper at the 7th International Hot Atom Chemistry Symposium in Juelich, then visiting laboratories and delivering lectures in Marburg, Bochum, Amsterdam (the Free University and the IKO), Saarbruecken, Freiburg, Geneva and Heidelberg. Over 3/4 of the lecture material was concerned with research carried out under the auspices of the United States Atomic Energy Commission. The lecture tour was sponsored by the scientific affairs division of the North Atlantic Treaty Organization, and did not consume AEC funds. From October through January the principal investigator was a Fulbright Lecturer at the Instituto Superior Tecnico of the Technical University of Lisbon, Portugal where he held a series of ca. 20 lectures on highly reactive species as chemical intermediates and also was invited to give several research seminars on AEC-sponsored work. Since January 9, the principal investigator has devoted ca. 25% of his time during the academic year to this project and 100% of three summer months. August has been spent at the Brookhaven National Laboratory working on the collaborative experiment on kinetics of atomic reactions studied in a discharge flow system carried out in cooperation with Dr. A. P. Wolf of the Department of Chemistry, Brookhaven.

REFERENCES

1. Progress report C00-1713-43 "Reaction Studies of Hot Silicon and Germanium Radicals," Peter P. Gaspar, principal investigator, August 31, 1973.
2. Y.-Y. Su, O.F. Zeck, S.H. Daniel and Y.-N. Tang, J. Chem. Soc., Chem. Comm., 637 (1973).
3. P.P. Gaspar, Rong-Juh Hwang and W.C. Eckleman, J. Chem. Soc., Chem. Comm., 242 (1974), C00-1713-40.
4. Y.-N. Tang, G.P. Gennaro and Y.-Y. Su, J. Amer. Chem. Soc., 94, 4355 (1972). These workers reported 1,1-difluoro[³¹Si]-1-silacyclopent-3-ene as the predominant product, constituting >95% of the observed volatile products.
5. Unpublished work of P. Markusch. See progress report C00-1713-20 "Reaction Studies of Hot Silicon and Germanium Radicals," Peter P. Gaspar, principal investigator, August 31, 1970, pp. 5-6.
6. H. Okonoshima, K. Yamamoto and M. Kumada, J. Amer. Chem. Soc., 94, 9263 (1972).
7. P.P. Gaspar, S.A. Bock and W.C. Eckelman, J. Amer. Chem. Soc., 90, 6914 (1968), C00-1713-3.
8. P.P. Gaspar and Rong-Juh Hwang, "Stereochemistry of a Silylene Addition Reaction," J. Amer. Chem. Soc., in the press, C00-1713-46.
9. P.P. Gaspar and G.S. Hammond, "Spin States in Carbene Chemistry" a chapter in Carbenes volume II, R.A. Moss and M. Jones, Jr., editors, John Wiley and Sons, N.Y., 1974, in the press.
10. P.S. Skell and E.J. Goldstein, J. Amer. Chem. Soc., 86, 1442 (1964), (two papers).
11. W.H. Atwell and D.R. Weyenberg, J. Amer. Chem. Soc., 90, 3438 (1968).
12. R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie and Academic Press, Weinheim, 1971, pp. 121-122.

13. M.R. Willcott and V.H. Cargle, J. Amer. Chem. Soc., 89, 723 (1967) and 91, 4311 (1969); P.H. Mazzocchi and H.J. Tamburin, ibid., 92, 7220 (1970).
14. E.A. Chernyshev, N.G. Komalenkova and S.A. Bashkirova, Dokl. Akad. Nauk SSSR, 205, 868 (1972).
15. (Si=C) M.E. Flowers and L.B. Gusel'nikov, J. Chem. Soc. (B), 419 (1968); T.J. Barton and E. Kline, J. Organometal. Chem., 42, C21 (1972); P. Boudjouk, J.R. Roberts, C.M. Golino and L.H. Sommer, J. Amer. Chem. Soc., 94, 7926 (1972); (Si=Si) D.N. Roark and G.J.D. Peddle, ibid., 94, 5837 (1972); (Ge=C) T.J. Barton, E.A. Kline and P.M. Garvey, ibid., 95, 3078 (1973); (Si=Si, Si=O, Si=C) T.J. Barton, and J.A. Kilgour, ibid., 96, 2278 (1974).
16. Progress report COO-1713-36, "Reaction Studies of Hot Silicon and Germanium Radicals," Peter P. Gaspar, principal investigator, August 31, 1972.
17. F.H. Field and J.L. Franklin, Electron Impact Phenomena, revised edition, Academic Press, 1970.
18. R. Wolfgang, Progress in Reaction Kinetics, G. Porter, editor, Pergamon, Oxford, 3, 63 (1965).
19. M. Marshall, C. MacKay and R. Wolfgang, J. Amer. Chem. Soc., 86, 4741 (1964).
20. G.G. Hess and F.W. Lampe, J. Chem. Phys., 44, 2257 (1966).
21. P. Potzinger and F.W. Lampe, J. Phys. Chem., 73, 3912 (1969).
22. J.M.S. Henis, G.W. Stewart, M.K. Tripodi and P.P. Gaspar, J. Chem. Phys., 57, 389 (1972), COO-1713-27.
23. T.-Y. Yu, T.M.H. Cheng, U. Kempter and F.W. Lampe, J. Phys. Chem., 76, 3321 (1972).
24. J.M.S. Henis, G.W. Stewart and P.P. Gaspar, J. Chem. Phys., 58, 3639 (1973), COO-1713-31.
25. G.W. Stewart, J.M.S. Henis and P.P. Gaspar, J. Chem. Phys., 57, 1990 (1972), COO-1713-28.

26. G.W. Stewart, J.M.S. Henis and P.P. Gaspar, J. Chem. Phys., 57, 2247 (1972), C00-1713-29.
27. J.M.S. Henis, G.W. Stewart and P.P. Gaspar, "Selective Hydrogen Elimination from Ion-Molecule Reaction Intermediates in Silane-Methane Mixtures," J. Chem. Phys., in the press, C00-1713-42.
28. G.W. Stewart, J.M.S. Henis and P.P. Gaspar, J. Chem. Phys., 58, 890 (1973), C00-1713-35.
29. P.S. Skell and P.W. Owen, J. Amer. Chem. Soc., 89, 3933 (1967) and 94, 5434 (1972).
30. M.D. Sefcik and M.A. Ring, J. Amer. Chem. Soc., 95, 5168 (1973).
31. E.P. Rack and A.A. Gordus, J. Chem. Phys., 34, 1855 (1961) and 36, 287 (1962).
32. M.D. Loberg and M.J. Welch, J. Amer. Chem. Soc., 95, 1075 (1973).
33. T.M.H. Cheng and F.W. Lampe, Chem. Phys. Lett., 19, 532 (1973).
34. M.D. Sefcik, J.M.S. Henis and P.P. Gaspar, "Silanium SiH_5^+ . The Protonation of Silane and the Chemistry of Silanium Ions Studied by Ion Cyclotron Resonance Spectroscopy," J. Chem. Phys., in the press, C00-1713-48.
35. H. Hartmann, L. Papula and W. Shrehl, Theoret. Chim. Acta, 17, 131 (1970).
36. V.L. Tal'rose and A.K. Lyubinova, Doklady Akad. Nauk SSSR, 86, 909 (1952).
37. A. Gamba, G. Morosi and M. Simonetta, Chem. Phys. Lett, 3, 20 (1969).
38. S. Ehrenson, Chem. Phys. Lett., 3, 585 (1969).
39. V. Kyczmons, V. Staemmler and W. Kutzelnigg, Chem. Phys. Lett., 5, 361 (1970).
40. M.D. Sefcik, J.M.S. Henis and P.P. Gaspar, "The Methanium Ion, CH_5^+ . Evidence for the Structure of a Non-classical Ion from Reaction Studies by Ion Cyclotron Resonance Spectroscopy," J. Chem. Phys., in the press, C00-1713-47.

41. P.P. Gaspar, A.D. Haizlip and K.Y. Choo, J. Amer. Chem. Soc., 94, 9032 (1972), C00-1713-30.
42. K.Y. Choo and P.P. Gaspar, J. Amer. Chem. Soc., 96, 1284 (1974), C00-1713-41.
43. P.P. Gaspar, C.-T. Ho and K.Y. Choo, "Organosilicon Iminamino Radicals from the Addition of Silyl Radicals to Diphenyldiazomethane," submitted to J. Amer. Chem. Soc. (June, 1974), C00-1713-45.
44. R.W. Fessenden, J. Chem. Phys. 58, 2489 (1973).
45. P.L. Timms, Advances in Inorganic Chemistry and Radiochemistry, 14, 121 (1973).
46. R. Kirk and P.L. Timms, J. Amer. Chem. Soc., 91, 6315 (1969).
47. P.P. Gaspar and J.J. Frost, J. Amer. Chem. Soc., 95, 6567 (1973), C00-1713-33.