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 mode of formation of silylene; b. Elucidation of the role of ionic reactions in the chemistry of recoiling silicon atoms; c. Kinetics of addition of silyl radicals to olefins; d. Flow-discharge kinetic measurements of the rates of reaction of $^2P_{3/2}$ and $^2P_{1/2}$ chlorine atoms with saturated and unsaturated substrates.

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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, 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. In order to accomplish these objectives, a fourth goal has been set: 4. To prepare by chemical means and to study the reactions of silicon and germanium electron deficient radicals and ions which are probable reactive intermediates in the recoil reaction systems.

This summary of research accomplishments during the past year covers the following topics: a. Primary reactions of recoiling silicon atoms and the mode of formation of silylene $^{31}\text{SiH}_2$. b. The role of ionic reactions in the chemistry of recoiling silicon atoms. c. Kinetics of silyl radical addition reactions. d. Flow-discharge experiments on the reactions of chlorine atoms.

Primary reactions of recoiling silicon atoms and
the mode of formation of silylene

It had previously been established¹ that $^{31}\text{SiH}_2$ is the principal reactive intermediate in the formation of the major products $^{31}\text{SiH}_4$ and $^{31}\text{SiSiH}_6$ from the reactions of recoiling silicon atoms in phosphine-silane mixtures. In the past year experiments were undertaken to determine the manner in which $^{31}\text{SiH}_2$ is formed from recoiling silicon atoms.

Two questions were posed: 1. Does a recoiling silicon acquire its hydrogen atoms one at a time, forming $^{31}\text{SiH}_2$ via ^{31}SiH or are both hydrogens

acquired in a single step? 2. Is hydrogen acquired by direct abstraction or does insertion occur into an H-R bond, followed by unimolecular dissociation of the insertion product?

insertion-dissociation:

The answer to the first question was obtained by studying the reactions of recoiling silicon atoms with a substrate $\text{HSi}(\text{CH}_3)_3$ which contains only a single labile hydrogen atom, it having been demonstrated that alkanes do not contribute to the formation of silylene. Skell has studied the reactions of thermally evaporated silicon with trimethylsilane and obtained 1,1,1,3,3,3-hexamethyltrisilane in 27% yield (14% when silicon was evaporated by electron bombardment).²

A consecutive insertion mechanism was postulated by Skell:

We find that fast-neutron irradiation of trimethylphosphine-trimethylsilane mixtures gives as the major product 1,1,1-trimethyldisilane, a product of silylene insertion.

In addition to the 1,1,1-trimethyldisilane, formed in ca. 8% absolute yield from 1:1 $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_3\text{SiH}$ mixtures, 1,1,1,3,3,3-hexamethyltrisilane was obtained in ca. 3% absolute yield. This product can be rationalized by the consecutive insertion mechanism proposed by Skell,² and by this group in connection with trisilane formation from reactions of recoiling silicon atoms with silane,¹ or instead by an ionic mechanism (vide infra). Other products obtained in small quantities from the reactions of recoiling silicon atoms in trimethylphosphine-trimethylsilane mixtures are silane, methylsilane, dimethylsilane, and, apparently, 1,1,1,2-tetramethyldisilane and 1,1,1,2,3,3,3-heptamethyltrisilane.

The formation of a silylene insertion product in a system containing no molecules with more than one labile hydrogen atom seems to prove that silylene can be formed by consecutive acquisition of single hydrogens by recoiling silicon atoms.

The yields of both 1,1,1-trimethyldisilane and 1,1,1,3,3,3-hexamethyltrisilane increase (to ca. 35 and 5% respectively) when phosphine PH_3 replaces trimethylphosphine in the reaction mixture. Only a small amount of this increase can be due, however to the formation of $^{31}\text{SiH}_2$ from PH_3 . In an independent experiment on the reactions of recoiling silicon atoms with phosphine-butadiene mixtures, a maximum yield of ca. 5% of silacyclopentene, the silylene insertion product is obtained.³

When silylene is produced by the pyrolysis of disilane in the presence of butadiene, a very high yield (>50%) of silacyclopentene is produced.³

This experiment supported the hypothesis that silacyclopentene in the recoil experiments is due to addition of silylene to butadiene, and more significantly, indicated that the low yield of silacyclopentene in the recoil experiments is due to the low yield of $^{31}\text{SiH}_2$ from the reaction of recoiling silicon atoms with phosphine. Professor Yi-Noo Tang has also observed a low yield of silacyclopentene from the reactions of recoiling silicon atoms in phosphine-butadiene mixtures.⁴

It is interesting to note that the yield of silacyclopentene from phosphine-butadiene mixtures goes through a maximum at ca. 10% butadiene concentration and then decreases with increasing mole fraction of butadiene. This indicates that butadiene can compete with phosphine in the primary reactions of silicon atoms, as well as reacting with silylene. Thus the decrease in silylene concentration with increasing butadiene, leads to a decrease in silacyclopentene yield. A product, thus far unidentified, becomes the major product from phosphine-butadiene mixtures at butadiene concentrations above 10% and increases monotonically with increasing butadiene concentration. This product is believed to be $\text{SiH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$, $\text{SiH}_3\text{CH}_2\text{CH}=\text{CH}-\text{CH}_3$ or $\text{SiH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$. The following kinetic scheme rationalizes the observed variation in product yields with substrate ratios:

The question whether the acquisition of hydrogens occurs by direct abstraction or instead by insertion followed by unimolecular dissociation was answered by a combination of experiments on the dependence of product yields on total pressure, and on moderator and scavenger concentrations.

It was found that the yield of 1,1,1-trimethyldisilane is not significantly decreased by an increase in pressure up to 7000 torr. However, the yield is significantly decreased at high moderator concentrations at pressures of ca. 3000 torr. This suggests strongly that unreactive collisions of silicon atoms before reaction are more effective at decreasing the yield of $^{31}\text{SiH}_2$ than is the increase in collision frequency and hence the deactivation rate of vibrationally excited silicon atom insertion products. The significant moderator effect in the absence of a pressure effect is in accord with a mechanism whereby silicon atoms at high kinetic energy (or in an excited electronic state) abstract hydrogen atoms bonded to silicon.

In the presence of large quantities of moderator the yield of 1,1,1,3,3,3-hexamethyltrisilane increases as the yield of 1,1,1-trimethyldisilane decreases. While this could be viewed as evidence for the occurrence of insertion product as a common intermediate in the formation of both disilanes (formed via silylene $^{31}\text{SiH}_2$) and trisilane,

scavenger experiments have shown this to be improbable. While the yield of 1,1,1-trimethyldisilane from the reactions of silicon atoms with trimethylsilane, and the yield of silane from the reactions of silicon atoms with silane are reduced ca. 50% and 40% respectively, in the presence of nitric oxide, the yields of the corresponding trisilanes are reduced by ca. 0 and

20% respectively. This indicates that different reaction sequences are responsible for the formation of disilanes and trisilanes, or that scavenging occurs after the branching point in a single reaction sequence. If consecutive insertion by silicon atoms is responsible for the formation of trisilane, then the lack of a scavenger effect implies that single divalent silicon species are not efficiently scavenged by nitric oxide. This in turn implies the occurrence of another kind of silicon species, such as an odd-electron species (or a triplet divalent species) along the reaction path leading to disilane products via silylene. The scavenger studies thus provide support for, if not proof of, a hydrogen abstraction mechanism for the formation of silylene.

If ionic rather than neutral reactions give rise to a substantial portion of the trisilane products in the reactions of recoiling silicon atoms with silanes, then the scavenger experiments simply confirm that a sequence of reactions involving neutral species gives rise to disilanes, entirely different from the ionic reactions which give rise to trisilanes.

The experiments on the reactions of recoiling silicon atoms in phosphine-trimethylsilane and trimethylphosphine-trimethylsilane mixtures was carried out by Mr. J. D. Holten III. The reactions of recoiling silicon atoms in phosphine-butadiene mixtures and the reactions of silylene with butadiene have been studied by Mr. Rong-Ju Hwang.

The Role of Ionic Reactions in the Chemistry of Recoiling Silicon Atoms

In the past 18 months we have outlined a possible reaction sequence for the formation of trisilane from the reactions of silicon ions with silane.⁵⁻⁸

The demonstration that such a sequence actually does contribute to the formation of trisilane in the recoil reaction systems has been more difficult than was indicated by the preliminary experiments.

An extensive series of experiments has been carried out employing a number of structurally related alkyl amines as additives to phosphine-silane mixtures prior to fast-neutron irradiation. As indicated in the following table, the ionization potentials of these amines span a range from ca. 0.6 eV below to ca. 2. eV above that of silicon.⁹

Et ₃ N	7.50 eV	Si	8.12
Et ₂ NH	8.01	SiH ₄	12.2
EtNH ₂	8.86	PH ₃	9.98
Me ₃ N	7.82	NO	9.25
Me ₂ NH	8.24		
MeNH ₂	8.97		
NH ₃	10.15		

Since the charge exchange reactions of Si⁺ with triethylamine and trimethylamine are exothermic, these amines can serve as ion scavengers provided that the charge exchange reactions are rapid and the amines do not react rapidly with the neutral silicon species present, including the reaction products.

The rate constant for electron transfer from triethylamine to Si⁺ was determined for thermal Si⁺ ions by ion-cyclotron resonance spectroscopy to be $30.75 \pm 5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, and is thus quite rapid.

The products from recoiling silicon atoms in phosphine-silane mixtures: silane, disilane and trisilane were shown to be stable toward triethylamine and trimethylamine in the gas phase.

When triethylamine and trimethylamine are present in phosphine-silane mixtures during fast-neutron irradiation the yield of radio active trisilane is sharply reduced in the presence of even 1 or 2% additive. The yields of silane and disilane are unaffected. This is the expected result if $^{31}\text{Si}^+$ ions are precursors of the trisilane product and are neutralized by charge exchange with the amines more rapidly than they react to form trisilane. Since no comparably efficient ionic pathway to the formation of silane and disilane was uncovered by our ion-cyclotron-resonance spectroscopic experiments, no decrease in the yields of these products was expected upon addition of amines.

Thus triethylamine and trimethylamine selectively scavenge a precursor of trisilane, but do not scavenge the precursors of silane and disilane. This is a complementary effect to the scavenging by nitric oxide, which reduces the yields of silane and disilane, much more than the yield of trisilane. The ionization potential of nitric oxide is greater than that of Si and thus rapid charge exchange between Si^+ and NO is not anticipated.

That the effect of triethylamine on the yield of trisilane is due to the nature of the precursor of the product rather than due to the nature of the product was demonstrated. Triethylamine was found to have a negligible effect on the yield of trisilane from phosphine-disilane mixtures, in which the trisilane product is formed by silylene insertion:

If the decrease in trisilane yield in the presence of triethylamine and trimethylamine is due to neutralization of $^{31}\text{Si}^+$ by charge exchange with the amine, the resulting neutral silicon atom must undergo silicon-hydrogen bond insertion at reduced rate or not at all.

It must be recalled that the ground state of the silicon atom is ${}^3\text{P}$ while the ground state of SiH_2 is a singlet, lying some 2 eV below the lowest energy triplet.¹⁰ Therefore insertion by ground state triplet silicon atoms into silicon-hydrogen to give triplet divalent silicon species is some 2 eV/mole less exothermic than the spin-forbidden insertion to give the singlet divalent silicon species. Thus our position is that singlet silicon atoms (${}^1\text{D}$ and ${}^1\text{S}$ lie ca. 1.5 and 2 eV above ${}^3\text{P}$) can undergo facile insertion into silicon-hydrogen bonds, but ground-state triplet silicon atoms cannot. Therefore a neutralization of ${}^{31}\text{Si}^+$ leading to ${}^3\text{P}^{31}\text{Si}$ will result in a decrease in trisilane yield. Therefore the formation of trisilane by consecutive insertion of silicon atoms into silicon hydrogen bonds of two silanes, as observed by Skell, is not precluded by our observation of a scavenging effect by triethylamine and trimethylamine. The trisilane yields do not fall to zero in the presence of even substantial concentrations of amines, perhaps indicating some contribution from neutral silicon atoms to the yield of trisilane in the recoil system. It is clear however, that the major path taken by neutral silicon atoms in phosphine-silane mixtures is the formation of silylene.

The comparatively clear picture of the effect of amines upon product yields from phosphine-silane mixtures is somewhat obscured when amines with ionization potentials higher than that of atomic silicon are employed as additives in recoil reaction mixtures.

Ammonia is found to cause some decrease in the yield of trisilane, but no decrease in the yields of silane and disilane. Thus ammonia scavenges a

precursor of trisilane, even though electron transfer from NH_3 to Si^+ is endothermic by some 2 eV. This could be explained by electron transfer to "hot" Si^+ or by a reaction other than electron transfer between Si^+ and NH_3 . Such a reaction was found by ion-cyclotron resonance spectroscopy.

Evidence that it is Si^+ which is being scavenged in the recoil systems comes from the observed similarity of the ratio of the efficiency of triethylamine and ammonia in reducing the trisilane yield and the ratio of the rate constants for electron transfer from Et_3N to Si^+ and the rate constant for reaction of Si^+ and NH_3 .

Another source of the scavenger effect, the reduction of trisilane yields by triethylamine, trimethylamine and ammonia would be the reaction of these amines with some silicon species other than Si^+ . This cannot be rigorously excluded at the present time. However, the lack of scavenger effect on the yields of silane and disilane indicates that none of the reactive intermediates involved in the formation of silane and disilane are scavenged by these amines. Since silicon atoms are believed to be involved in the formation of silane and disilane, and since the intermediates in silane and disilane formation suffer scavenging by NO, while the intermediates in trisilane formation are scavenged to a lesser extent, it does not appear to be silicon atoms or divalent or trivalent neutral silicon species which are scavenged by amines.

The other amines, mono- and diethylamine and mono- and dimethylamine, all with higher ionization potentials than silicon atoms, all cause some decrease in the trisilane yield from reactions of recoiling silicon atoms in phosphine-silane mixtures. At amine concentrations above 10% some reduction

of disilane yield is observed and, in the case of mono- and dimethylamines, the silane yield increases slightly. These observations are explained by reactions of Si^+ (other than simple charge exchange) with amines containing N-H bonds leading to a reduction of the trisilane yield from the ionic pathway. The reduction of disilane yield implies a reaction of $^{31}\text{SiH}_2$ with N-H bonds, either directly or via an ylid intermediate.

Silylamines are unstable and decomposition could account for the slightly enhanced silane yields.

Ion-cyclotron-resonance experiments indicate that silicon ions undergo efficient ion-molecule reactions with phosphine. Therefore the involatile activity (ca. 30%) left on the walls of reaction ampoules in the reactions of recoiling silicon atoms with 1:1 phosphine-silane mixtures may also represent contributions from silicon ions. If this were the case the total ionic contribution would be ca. 1/3 of the total reactions in which the silicon recoiling from $^{31}\text{P}(\text{n},\text{p})^{31}\text{Si}$ takes part.

In addition the ion-molecule reactions already reported in this section, further studies have been carried out on the reactions of SiH_2^+ with methane, previously reported.¹¹

It had been deduced that this reaction proceeds via a long-lived intermediate from the observation that H is lost in preference to D in the reaction of SiH_2^+ with CD_4 . We have now ruled out an isotope effect as the source of

this observation by carrying out the isotopic mirror image experiment. A relatively long-lived intermediate was confirmed by the observation of preferential loss of deuterium over hydrogen in the reaction of SiD_2^+ with CH_4 . Thus loss of the more weakly bound hydrogens attached to silicon is preferred to loss of carbon-bound hydrogen.

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

Kinetics of Silyl Radical Addition Reactions

The failure of small quantities of ethylene to drastically reduce the yields of silane and disilane from the reactions of recoiling silicon atoms in phosphine-silane mixtures has been one of the pieces of evidence used to preclude silyl radicals $^3\text{SiH}_3$ from a major role in this reaction system.¹ However it is only in the past year that the critical assumption that silyl radicals add rapidly to ethylene has been tested quantitatively. The adduct of a silyl radical and ethylene was observed by ESR spectroscopy by Krusic and Kochi, who did not, however, study the rate of reaction.¹²

We too have detected this adduct and used the flash-photolysis-electron spin resonance technique previously applied to the rate of dimerization of silyl radicals¹³ to study the rate of this reaction. The addition of unsubstituted silyl radicals to ethylene is so rapid that accurate rate measurements were not possible. It was possible however to measure the rate of addition of trimethyl silyl radicals to ethylene. See technical report COO-1713-41.

Even this reaction is so rapid that with a solution ca. 10^{-5} molar in trimethylsilyl radicals and 10^{-2} molar in ethylene, the half-life of the reaction is less than one millisecond at 20° C. From the rate constant for pseudo-first-order decay of the trimethylsilyl radical and the concentration of ethylene, the second-order rate constant for the addition reaction was computed. Measurements were made over the temperature range -74 to $+20^{\circ}$ C and a satisfactory Arrhenius plot constructed whose slope and intercept yielded the activation parameters $E_a = 2.5 \pm 0.2$ Kcal/mole and $\log A = 7.0 \pm 0.2$ ($1 \text{ mole}^{-1} \text{ sec}^{-1}$). This preexponential factor lies in the same range as that for the addition of carbon-centered radicals to ethylene. The activation energy for addition of the silyl radical is considerably lower than that for addition of carbon-centered radicals ($E_a = 6.8$ Kcal/mole for addition of methyl radicals to ethylene), and therefore the addition of silyl radicals is more rapid.

While the rates of addition of carbon-centered free radicals to olefins have been studied by various workers using indirect means to determine rate constants, and recently such a method has been used to measure the rate of addition of disilanyl radicals to ethylene,¹⁴ we believe that our experiments represent the first rate measurement for a Group IV radical addition reaction employing direct monitoring of changes in radical concentrations with time by kinetic spectroscopic techniques.

The addition of trimethylsilyl radicals to a number of other olefins was investigated with the hope that a slower addition reaction could be found. In all cases studied the addition was rapid, offering no advantage for kinetic studies over the addition to ethylene itself. The ESR spectra of addition products not previously reported were described in Dr. Choo's dissertation (technical report C00-1713-39).

The present kinetic measurements indicate that ethylene should be a highly effective scavenger for silyl radicals in silane reaction mixtures, although, as indicated by our previous work, ethylene cannot scavenge hydrogen atoms in silane reaction systems.¹⁵

A phase shift technique was used to measure a very controversial reaction rate, the rate of hydrogen abstraction from trimethylsilane by tertiary-butoxy radicals.

A value for k of $3 \times 10^2 \text{ l mole}^{-1} \text{ sec}^{-1}$ was obtained.

The experiments in this section were carried out, brilliantly, by Mr., now Dr. Choo and are reported in his doctoral dissertation (technical report COO-1713-39).

Flow-Discharge Experiments on the Reactions of Chlorine Atoms

As part of the program for the development of a discharge-flow system for the measurement of carbon, silicon and germanium atom reaction rates, both vacuum ultraviolet atomic absorption and atomic fluorescence detection were employed to measure the rates of reaction of $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ chlorine atoms with various substrates. It was of interest to measure simultaneously rates of reaction of both electronic states of the chlorine atom with the same sub-

strate, since we shall measure reaction rates for several states of carbon, silicon and germanium atoms.

The rates of chlorine atom reactions have been studied extensively, but mostly by indirect competition methods which do not distinguish between the two lowest electronic states¹⁶ since the $^2P_{1/2}$ state of chlorine lies only 2.5 Kcal/mole above the ground $^2P_{3/2}$ state, both states may be formed under a variety of conditions. Recently Callear and coworkers have observed considerable differences in reactivity between $^2P_{1/2}$ and $^2P_{3/2}$ iodine atoms, which are, however, separated in energy by 21.7 Kcal/mole.¹⁷ Direct study of ground state $^2P_{3/2}$ chlorine atom reaction rates by flow-discharge-ESR¹⁸ and flash photolysis-atomic fluorescence techniques¹⁹ have been reported.

Electronically excited $^2P_{1/2}$ chlorine atoms were directly detected by Carrington and coworkers using a flow-discharge-ESR technique and the population ratio of $^2P_{1/2}$ to $^2P_{3/2}$ chlorine atoms was found to exceed the Boltzmann factor.²⁰ Clyne and Cruse also detected $^2P_{1/2}$ chlorine atoms in a discharge flow system with atomic absorption detection, but reported no reaction studies.²¹ In the only published report on the reaction rates for $^2P_{1/2}$ chlorine atoms, employing a flash photolysis-vacuum ultraviolet absorption technique, the rates of reaction of $^2P_{1/2}$ chlorine atoms with several substrates were reported to be several orders of magnitude more rapid than the analogous reactions of $^2P_{3/2}$ ground state chlorine atoms, which were however determined in separate experiments.²²

In our experiment we determined the $^2P_{1/2}$ to $^2P_{3/2}$ ratio for chlorine atoms produced in a microwave discharge in chlorine-doped helium at 20 torr to be 3 to 10×10^{-2} , as compared to the equilibrium ratio (at 300° K) of 7×10^{-3} . Thus there is a fairly sizable contribution (3 to 10%) of excited chlorine atoms to reactions carried out under these conditions.

Spurious sources for the apparently enhanced population of excited chlorine atoms were considered and eliminated. That the ratio of $^3P_{1/2}$ to $^3P_{3/2}$ chlorine atoms is not at equilibrium was demonstrated by change of the observed ratio with flow conditions at constant temperature.

The rate constants for reactions of both states of the chlorine atom with various substrates measured simultaneously in our experiments is given in the table below together with available literature values. Our rate constants for ground state chlorine atom reactions are in reasonable agreement with the published values. In the two cases where comparison is possible for the excited $^2P_{1/2}$ state, our rate constants are very much lower than the published values. In reactions with saturated substrates, i.e. where abstraction takes place, we find excited $^2P_{1/2}$ chlorine atoms react slightly faster than ground state $^2P_{3/2}$ chlorine atoms. In addition reactions with olefins, the trend is reversed, $^2P_{1/2}$ reacts ca. 1/3 as rapidly as $^2P_{3/2}$. That it is chemical reactions of the excited chlorine atoms which cause a decay in the $^2P_{1/2}$ chlorine atom concentration, rather than physical relaxation, is clearly indicated by the parallelism for both $^2P_{1/2}$ and $^2P_{3/2}$ of rate of decay with substrate structure. Since it must be chemical reaction that destroys the ground state, it is reasonably inferred that it is chemical reaction which is responsible for removal of the excited state. Atomic fluorescence experiments gave on the whole results in agreement with those obtained using atomic absorption detection.

One fascinating discrepancy between the results from atomic absorption and atomic fluorescence detection of chlorine atoms is the apparent enhancement of the concentration of higher $^2P_{3/2}^0$ chlorine atoms during reactions of the two lowest state chlorine atoms. This enhancement of excited state concentration is of obvious interest, since a true population inversion might

Rates of reactions of Cl atoms

Substrate	Cl($^2P_{3/2}$)		Cl($^2P_{1/2}$)	
	k(cc/molecule sec)		k(cc/molecule sec)	
	This work	reference ^e	This work	reference
H ₂	1.7 x 10 ⁻¹⁴	1.2, ^a 1.4 ^b	2.7 x 10 ⁻¹⁴	7 x 10 ⁻¹² ^d
D ₂	1.7 x 10 ⁻¹⁵	1.3 ^a	3.3 x 10 ⁻¹⁵	
cyclopropane	3.8 x 10 ⁻¹³	0.8 ^a	6.5 x 10 ⁻¹³	
CH ₃ Cl	4.9 x 10 ⁻¹³	3.0 ^a	8.4 x 10 ⁻¹³	
CH ₃ F	4.7 x 10 ⁻¹³		7.8 x 10 ⁻¹³	
CH ₄	2.6 x 10 ⁻¹³	0.6, ^a 1.5 ^b	2.8 x 10 ⁻¹³	
CH ₂ -CH ₂	2.6 x 10 ⁻¹²	3.3 ^c	0.8 x 10 ⁻¹²	
CH ₂ =CHCl	2.5 x 10 ⁻¹²	3.3	0.4 x 10 ⁻¹²	
t-CHCl=CHCl	3.9 x 10 ⁻¹²	4.0	1.3 x 10 ⁻¹²	
c-CHCl-CHCl	3.8 x 10 ⁻¹²	6.0	1.1 x 10 ⁻¹²	
Cl ₂	<4 x 10 ⁻¹³		<4 x 10 ⁻¹³	
CCl ₄	<5 x 10 ⁻¹³		<5 x 10 ⁻¹³	5 x 10 ⁻¹¹ ^d

^aCalculated from "Tables of Bimolecular Gas Reactions," A.F. Trotman-Dickenson and G.S. Milne, NSRDS-NBS 9.

^bReference 19.

^cJ. Knox and K.C. Waugh, Trans. Far Soc. 65, 1585 (1969).

^dReference 22.

^eAll the rate constants are of the same orders of magnitude as our values.

form the basis of a vacuum ultraviolet chemical laser.

The availability of a pair of electronic states of the same atom, differing by only $2\frac{1}{2}$ Kcal/mole in electronic energy, provides an interesting opportunity to study the influence of small differences in electronic structure and coupling of angular momentum on chemical reactivity and physical collision processes.

The experiments of this section were carried out by Mr. (now Dr.) Choo and are reported in his dissertation (COO-1713-39).

PERSONNEL

I can only praise the imagination, skill and effort of my coworkers. After about 18 months in Saint Louis, Dr. Gerald Stewart moved to Cambridge, Mass. to accept a postdoctoral appointment to work in molecular beams kinetics with Dr. John Ross at MIT. This opportunity came rather suddenly and Dr. Stewart left some six months prematurely. However his contribution to seven papers (four published, one submitted for publication, one in preparation) has substantially enhanced our understanding of the role of ionic reactions in silicon atom recoil chemistry. Mr. Dewey Holten graduated with honors this June, having spent three undergraduate years contributing to this research program. Mr. Holten, like his predecessor Mr. Frost, was awarded the John Sowden Memorial Prize as the outstanding senior chemistry major by the Washington University Chemistry Department. Mr. Holten is entering graduate school in chemistry at the University of Washington, Seattle. Mr. Holten is a coauthor of one paper which has already appeared and two in preparation.

Fortunately, outstanding successors have been found for both Dr. Stewart and Mr. Holten. Dr. Michael Sefcik comes to this project after completing his Ph.D. at San Diego State University, having worked on the reactions of thermally generated divalent silicon and germanium species with Professor M. A. Ring, one of the outstanding contributors to the understanding of the physical inorganic chemistry of silanes and germanes. Dr. Sefcik spent four weeks in St. Louis in the spring and is returning in the middle of August to begin full-time work.

For the past six months Mr. Holten and Mr. Hwang have been training a new undergraduate research assistant, Mr. Barry Mizes. Mr. Mizes has already demonstrated that he has the intellectual and technical ability, and more

important the interest in and enthusiasm for the work in recoil chemistry he has undertaken.

Dr. Kwang Yul Choo received his Ph.D. this spring after four years of intensive and brilliant experimentation on the rates of reactions of various short-lived intermediates important for the understanding of silicon recoil chemistry. Dr. Choo is coauthor of two papers which have already appeared, and two more which have been submitted for publication. He was offered several postdoctoral fellowships, including a Canadian National Research Council Fellowship, a singular honor. Dr. Choo chose to accept a postdoctoral position with Dr. Sidney Benson in the department of thermochemistry and reaction kinetics of the Stanford Research Institute.

A fine graduate student Mr. Rong-Juh Hwang has completed his second year of graduate work, employing unsaturated hydrocarbons as probes for the primary and secondary reactions of recoiling silicon atoms.

PUBLICATIONS

Five papers have appeared in the last twelve months:

1. COO-1713-28 "Ion Molecule Reactions in Silane-Methane Mixtures" by G.W. Stewart, J.M.S. Henis and P.P. Gaspar, J. Chem. Phys., 57, 1990 (1972).
2. COO-1713-29 "Hydride-Ion Transfer and Isotope Effects in CD₄-Silane Ion Molecule Reactions" by G.W. Stewart, J.M.S. Henis and P.P. Gaspar, J. Chem. Phys., 57, 2247 (1972).
3. COO-1713-30 "The Disappearance of Silyl Radicals in Silane. A Flash Photolysis-ESR Kinetic Study" by Peter P. Gaspar, Allene D. Haizlip and Kwang Yul Choo, J. Amer. Chem. Soc., 94, 9032 (1972).
4. COO-1713-31 "Endothermic Ion-Molecule Reactions in Silane" by J.M.S. Henis, G.W. Stewart and P.P. Gaspar, J. Chem. Phys., 58, 3639 (1973).
5. COO-1713-35 "Implications of Ion-Molecule Reactions for Recoil Silicon Studies" by G.W. Stewart, J.M.S. Henis and P.P. Gaspar, J. Chem. Phys., 58, 890 (1973).

There are two papers 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 Transformation in Solids, G. Harbottle and A.G. Maddock, editors, North Holland, Amsterdam, in the press.
2. 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., in the press.

Four additional papers have been submitted for publication:

1. COO-1713-37 "Rates of Reaction of Hydrogen Atoms with Silane and Germane" by Kwang Yul Choo, Peter P. Gaspar, and A.P. Wolf, submitted to Faraday Transactions I.
2. COO-1713-40 "Reactions of Recoiling Silicon Atoms with Phosphine and Butadiene, and a New Trap for Silylene" by Peter P. Gaspar, Rong-Juh Hwang and William C. Eckelman, submitted to Chemical Communications.
3. COO-1713-41 "The Addition of Trimethylsilyl Radicals to Ethylene. A Flash Photolysis-ESR Kinetic Study" by Kwang Yul Choo and Peter P. Gaspar, submitted to J. Amer. Chem. Soc.
4. 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, submitted to J. Chem. Phys.

Finally an important technical report is Dr. Choo's dissertation:

COO-1713-39 "Part 1. Reactions of Reactive Silicon Species. Part 2. Reactions of $\text{Cl}(^2\text{P}_{3/2})$ and $\text{Cl}(^2\text{P}_{1/2})$ Species" by Kwang Yul Choo.

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1973.

(Degree granted June 2, 1972.)

STATEMENT OF EFFORT

During the preceding twelve months the principal investigator has devoted approximately 25% of his time during the academic year to this project and 100% of two summer months. He will be in Europe for four months this fall and early winter, spending September in Germany delivering an invited paper at the 7th International Hot Atom Chemistry Symposium in Jülich, and lecturing at the Universities of Marburg, Bochum, Saarbrücken, Freiburg, Heidelberg, Göttingen, and Amsterdam (Holland). October, November and December will be spent as Fulbright Lecturer at the Instituto Superior Technico, Lisbon, Portugal. The progress of the research carried out under the auspices of the United States Atomic Energy Commission will provide a substantial proportion of the lecture material.

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