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Silicon and Germanium Atoms. Recoil Chemistry*

MASTER

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In the presence of so many renowned hot-atom chemist I am reluctant to talk about our work because I am very aware of the short distance we have travelled toward our goals. We hope by studying the reactions of very simple silicon and germanium radicals to better understand the influence of electronic structure and kinetic and internal energy on chemical reactivity. We have chosen to study the reactions of very simple species first because their chemistry is novel and interesting in itself, second because simple free radicals are amenable to more or less exact theoretical treatment, and finally because the molecular spectra of simple radicals can be exactly analyzed and can, when available, provide information about structure and energy of these species.

Let me tell you first how I became interested in the chemistry of electron-deficient radicals. I was about eight years old when, in 1944, I read about a marvelous reaction in the periodical literature. It is shown in the form I first saw it on the first slide. Later my interest was extended to the silicon and germanium radicals whose structures resemble those of the simple carbon species.

We decided to approach the problem of studying simple silicon and germanium radicals by producing high-energy silicon and germanium atoms by nuclear techniques. We were confident that the primary reactions of the recoiling atoms would produce the other radicals of interest to us: SiH , SiH_2 , SiH_3 , GeH , GeH_2 and GeH_3 . Let me briefly outline our approach.

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First, since we are entering an unknown area of chemistry - little work has been done on silicon and germanium atoms and radicals - we must determine what reactions take place. Second we must begin to elucidate the operative reaction mechanisms, at least to the extent of determining what are the reactive intermediates in the reaction sequence which produces the observed products. Then we can begin to learn the details of elementary reaction processes - what are the energetics, the activation parameters and steric requirements of the transformations of various simple silicon and germanium radicals. Only then can we hope to begin answering the fundamental questions which we have posed ourselves. We have not reached this latter stage, but we are making progress toward this end.

Let us talk about what we have done. We produce silicon and germanium atoms in the gas-phase by fast-neutron bombardment of the appropriate precursor nuclei. The nuclear reactions and the recoil energies and half-lives of the product atoms are shown on the second and third slides. The phosphorus is in the form of gaseous phosphine PH_3 , the germanium in the form of gaseous germane GeH_4 , of natural isotopic abundance. Phosphorus is of course monoisotopic. The high recoil energy insures that all bonds in the precursor molecules are broken. The long cascade downward in energy from the high initial values down to the few electron volts which is regarded as the upper limit for bond-forming reactions of hot atoms, this cascade is assumed to insure that in gaseous mixtures of low average ionization potential that the recoiling silicon and germanium atoms are electronically neutralized before chemical reactions can take place.

We have looked fairly carefully at the reactions of recoiling silicon atoms in phosphine-silane mixtures. In pure phosphine silicon atoms produce silane SiH_4 as sole volatile radioactive product, and only in low absolute yield - some 2%. In the presence of non-radioactive silane, however, silicon atoms react to give radioactive disilane Si_2H_6 as well as silane. The absolute yields are given

on the fourth slide as functions of the silane concentration. Quite high combined product yields are obtained - some 80% at 80% silane concentration. The more-or-less linear yield curves imply a competition between reactions of silicon atoms with silane which produce radioactive silane and disilane, and reactions of silicon atoms with phosphine which produce principally involatile products together with a little silane.

Knowing what products are formed from the reactions of silicon atoms with phosphine silane mixtures and how the yields vary with the composition of the reaction mixture, we are still not in a position to deduce a detailed reaction mechanism. We can however write down a simple kinetic scheme which rationalizes the data presented.

The fifth slide shows a set of product-determining steps, and expressions derived from them. By using the phrase "product-determining steps" we are begging the question whether these are really elementary reaction processes producing the indicated products in single fruitful encounters, or whether they are simply branch points in the mechanism. In the latter case the arrows serve as ellipses for several consecutive elementary steps. We note that the four steps include a single common intermediate, symbolized by X.

Of the three expressions derived from the kinetic scheme the third has already been demonstrated, since the absolute yield of radioactive disilane does appear to be a linear function of the silane concentration. We will now demonstrate the approximate validity of the second and third expressions giving respectively the inverse of the absolute yield of radioactive disilane and the yield ratio of silane to disilane as linear functions of the phosphine-silane ratio. The sixth slide shows that the reciprocal of the absolute yield of disilane is linear over a considerable range of phosphine-silane ratios. We concede that the deviation at the higher end may be real. The seventh slide indicates that the

yield ratio appears to be, granting considerable scattering of the data, a linear function of the substrate ratio.

Well, what this says is that the simple kinetic scheme may be correct, although an infinite number of more complicated schemes would give the same expressions for the yields. Even if the simple scheme is right we must determine the identity of the single kinetically important intermediate X.

We have attempted to identify X by a series of scavenger experiments. The eighth slide shows the effects of various scavengers on the absolute and relative yields of silane and disilane from the reactions of recoiling silicon atoms with 1:1 phosphine-silane mixtures. It can be seen that ethylene, carbon tetrafluoride, nitric oxide and hydrogen were all ineffective in changing the yields, absolute or relative, of the volatile products. We interpret the failure of these substances to act as scavengers as indicating that the active intermediate is not the thermal energy radioactive silyl radical SiH_3 . In this interpretation we rely heavily on analogy and other workers, unsubstantiated speculations. One would expect nitric oxide to scavenge a free radical like SiH_3 efficiently, but of course one does not really know the rate of reaction of silyl radicals with nitric oxide. It has been alleged that silyl radicals undergo facile addition to ethylene, as shown on the ninth slide, but no direct evidence was presented for the intervention of silyl radicals in the addition of silane to ethylene.

We are limited in our ability to interpret our own scavenger experiments by a lack of knowledge of the thermal chemistry of simple silicon radicals. Since we began our recoil atom experiments with the hope that we would shed light on the behavior of these species, we are caught in a cycle of circular ignorance. We are attempting to escape this trap by generating individually the simple radicals SiH , SiH_2 and SiH_3 which are possible intermediates, and studying their behavior under the conditions of the hot-atom experiments.

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We believe that the active intermediates in the product-determining steps is silylene SiH_2 , the silicon analog of methylene. Our scavenger experiment indicating that nitric oxide is not effective as a scavenger supports this hypothesis in light of the recent results of Strausz and Gunning. They claim that methyl-silylene, which also is not scavenged by nitric oxide, inserts into the silicon-hydrogen bonds of methylsilane. Their mechanism for the vacuum-ultraviolet photolysis of methylsilane is shown on the tenth slide. Our mechanism for the formation of disilane in the reaction of silicon atoms with phosphine-silane mixtures is shown on the 11th slide, and is completely analagous with Gunning's mechanism

Support for our belief in the intermediacy of SiH_2 also comes from the reactions of silicon atoms with phosphine-ethylene mixtures. While ethylene in low concentrations is a poor scavenger, 1:1 mixtures of phosphine and ethylene do give products incorporating ethylene. The major product has been tentatively identified as beta-silylethylphosphine, for whose formation we propose the mechanism shown on the 12th slide. It is significant that the major product of free-radical addition of silane to ethylene, which we showed in a previous slide to be ethylsilane, is only a very minor product in the recoil experiment.

We have shown by competition experiments that the same intermediate is responsible for the formation of this major product from the reaction of silicon atoms with phosphine-ethylene mixtures as is responsible for the formation of silane and disilane from the reactions of silicon atoms with phosphine-silane mixtures. We believe this intermediate to be SiH_2 in both cases.

Turning briefly to germanium atoms, it should be stated that our initial results indicate that the reactions of germanium atoms are very similar to those of silicon atoms. The 13th slide indicates that germanium atoms give analagous products in reactions with germane to the products of reaction of silicon atoms with silane. Not only are the products similar, but the product ratios are, within

experimental error, identical at the high pressure limit.

When silane-germane mixtures are irradiated with fast neutrons, a third product, germysilane is formed in addition to radioactive germane and digermane. On the 14th slide are given the absolute yields (in arbitrary units) as a function of the silane concentration. The total pressure was held constant at two atmospheres.

A series of product-determining steps for the reactions of germanium atoms with germane-silane mixtures similar to the scheme proposed for the reactions of silicon atoms with phosphine-silane mixtures is shown on the 15th slide. I will not take your time in showing the data which are in seeming agreement with the expressions derived from this kinetic scheme and shown at the bottom of the slide. Suffice it to say that all the steps are necessary, including the second step, the reaction of X with silane to form germane. This explains the observed increase in germane-digermane ratio observed with increasing silane concentration. We believe X to be $^{75}\text{GeH}_2$.

I have said nothing about the energies at which the recoiling silicon and germanium atoms undergo their primary reactions. There are large moderator effects suggesting the incursion of hot reactions somewhere in the reaction sequences. As a single example let us see the effect of added argon on the yield of radioactive silane from 1:1 phosphine-silane mixtures (16th slide). Similar large effects are found with neon moderator on silicon and to a lesser extent germanium atoms. In spite of the promise of the abstract, we have no explanation at this time for these moderator effects which seem so large as to be barely credible.

Let me summarize by saying that we have found the reactions of silicon and germanium atoms to be quite specific. Our results suggest that a single kinetically important intermediate may be involved in the reactions observed for each element. The identities of these kinetically important intermediates are not yet absolutely

certain, but we believe them to be the silicon and germanium analogs of methylene, SiH_2 and GeH_2 . We are happy to have made a beginning, but we are profoundly aware of what a great deal remains to be done. My heartfelt thanks go to my coworkers at Washington University - Dr. Eckelman, Mr. Bock, Mr. Frost, Mr. Levy, and to the United States Atomic Energy Commission, without whose financial support this work would have been impossible.

Si^{31} RECOIL ENERGY

CA 6×10^5 ev.

Si^{31} HALF-LIFE 2.62 HR.

^{75}Ge Recoil Energy $\sim 4 \times 10^4$ ev.

^{75}Ge Half-Life - 82 min.

$$\frac{1}{\text{absolute yield } \text{H}_3^{31}\text{SiSiH}_3} = \frac{\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4}{\sigma_1} \cdot \frac{[\text{PH}_3]}{[\text{SiH}_4]}$$

$$\text{and } \frac{[{}^{31}\text{SiH}_4]}{[\text{H}_3^{31}\text{SiSiH}_3]} = \frac{\sigma_2 + \sigma_3}{\sigma_1} \cdot \frac{[\text{PH}_3]}{[\text{SiH}_4]}$$

Further, absolute yield $\text{H}_3^{31}\text{SiSiH}_3$
 (for concentrations expressed as
 mole fractions, i.e. $[\text{PH}_3] = 1 -$
 $[\text{SiH}_4]$)

$$= \frac{\sigma_1 [\text{SiH}_4]}{(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) [\text{SiH}_4] + \sigma_3 + \sigma_4}$$

Effect of Scavengers on Product Yields from Fast-NeutronIrradiation of 1:1 Phosphine-Silane Mixtures^a

Experiment	Scavenger	Total Volatile Activity per Unit of Precursor	$\text{H}_3^{31}\text{SiSiH}_3/^{31}\text{SiH}_4$
1 ^b	none	300 ^c ± 50	4.4 ± 0.8
1	none	340 ± 60	5.2 ± 1.0
1	4% C ₂ H ₄	260 ± 40	4.5 ± 0.9
1	4% CF ₄	320 ± 50	6.2 ± 1.2
2	none	1600 ± 300	4.5 ± 0.9
2	none	2400 ± 400	5.2 ± 1.0
2	4% C ₂ H ₄	2200 ± 400	5.2 ± 1.0
2	4% C ₂ H ₄	1400 ± 200	4.3 ± 0.8
3	none	150 ± 30	4.9 ± 0.9
3	4% CF ₄	150 ± 30	4.6 ± 0.9
3	4% CF ₄	130 ± 20	4.9 ± 0.9
4	none	d	6.1 ± 1.2
4	50% NO	d	6.1 ± 1.2
4	50% H ₂	d	5.2 ± 1.0

STRAUSZ, OBE, AND DUHOLKE, JACS, 90, 1359 (1968)

$$\frac{\text{H}_3^{75}\text{GeGeH}_3}{^{75}\text{GeH}_4} = 5.0 \pm 0.8 \frac{^{75}\text{GeH}_4 + \text{H}_3^{75}\text{GeGeH}_3}{\text{TVA}} = 1.0 \pm 0.2$$

$$\frac{\text{H}_3^{31}\text{SiSiH}_3}{^{31}\text{SiH}_4} = 4.8 \pm 0.9 \frac{^{31}\text{SiH}_4 + \text{H}_3^{31}\text{SiSiH}_3}{\text{TVA}} = 0.97 \pm 0.16$$

$$\frac{1}{[{}^{75}\text{GeH}_3\text{SiH}_3]_{\text{abs}}} = \frac{k_2 + k_4 + k_6}{k_4} + \frac{k_1 + k_3 + k_5}{k_4} \cdot \frac{[\text{GeH}_4]}{[\text{SiH}_4]}$$

$$\frac{1}{[{}^{75}\text{GeH}_3\text{GeH}_3]_{\text{abs}}} = \frac{k_1 + k_3 + k_5}{k_3} + \frac{k_2 + k_4 + k_6}{k_3} \cdot \frac{[\text{SiH}_4]}{[\text{GeH}_4]}$$

$$\frac{[{}^{75}\text{GeH}_4]}{[{}^{75}\text{GeH}_3\text{GeH}_3]} = \frac{k_1}{k_3} + \frac{k_2}{k_3} \cdot \frac{[\text{SiH}_4]}{[\text{GeH}_4]}$$