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PROGRESS REPORT

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MASTER

REACTION STUDIES OF HOT SILICON RADICALS*

United States Atomic Energy Commission Contract No. AT(11-1)-1713

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During the past fifteen months we have successfully persued the research goals included in the scope of the contract; that is: 1. The chemistry of recoil silicon and how these reactions take place, 2. Determining the vibrational excitation and rates of rearrangement, and 3. Exploration of the reactions of atomic silicon with further reaction substrates.

In the past year the principal effort has been the elucidation of the reaction mechanism of the reactions of silicon atoms recoiling from the nuclear transformation $^{31}\text{P}(n,p)^{31}\text{Si}$ with phosphine, silane and ethylene.

Measurements of the absolute yields of the two volatile radioactive products ($^{31}\text{SiH}_4$ and $\text{H}_3^{31}\text{SiSiH}_3$) from phosphine-silane mixtures indicate that the product yields increase linearly with the concentration of nonradioactive silane. This suggests that there is a competition for one or more recoiling silicon species between an efficient reaction with silane which produces $^{31}\text{SiH}_4$ and $\text{H}_3^{31}\text{SiSiH}_3$ and processes which produce involatile products from reactions with phosphine. The product ratio increases rapidly with silane concentration until a plateau value of $\text{H}_3^{31}\text{SiSiH}_3 : ^{31}\text{SiH}_4 = 4.8 \pm 0.9$ is reached at ca. 20% silane. This indicates that reactions of recoiling silicon species which lead to the formation of volatile products are much more efficient with silane than with phosphine. The absolute and relative yield data can be accomodated by a kinetic scheme in which a single species reacts with silane and phosphine to give $^{31}\text{SiH}_4$, with silane to give $\text{H}_3^{31}\text{SiSiH}_3$,

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and with phosphine to give involatile products. This kinetic scheme, involving a single reactive intermediate in the product-determining steps is:

A large moderator effect - a decrease in product yields with added neon - indicates either that there is a "hot" reaction involving an excited precursor to the intermediate X in the kinetic scheme, or that X itself is being moderated, and the product-determining steps themselves are "hot" reactions. It is not feasible to decide between these two interpretations of the moderator experiments at this time. Studies of the effects of total pressure on the product yields will help determine which steps in the reaction scheme involve excited species.

Ethylene has been found to compete with silane for a common reactive intermediate. The major product from the fast-neutron irradiation of phosphine-ethylene mixtures has been tentatively identified as 3-silapropylphosphine $^{31}\text{SiH}_3\text{CH}_2\text{CH}_2\text{PH}_2$. This product is believed to arise by the following mechanism:

While an attractive possibility for the identity of the reactive intermediate X in the kinetic scheme proposed above is $^{31}\text{SiH}_2$, attempts to positively identify the reactive intermediates have been hampered by the scarcity of knowledge about the ground-state chemistry of simple silicon species such as SiH, SiH₂ and SiH₃.

The lack of reduction of product yields by scavenger quantities of NO, CF₄ and

C_2H_4 suggest that $^{31}SiH_3$ is not an important intermediate in the phosphine-silane and phosphine-ethylene systems. It is difficult at this time, however, to choose among Si, SiH and SiH₂ as product-determining intermediates. Free silicon atoms are obviously involved in the reaction schemes but it has not been determined whether they are involved in the product-determining steps.

The reactions of recoiling silicon atoms with phosphine-butadiene mixtures have been found to produce several products which appear to contain a PH₂-group. Apparently the primary products, which may contain silacyclopropane rings, react with phosphine to form the observed stable products. Product identities are being established and conditions are being sought under which primary products such as silacyclopropane can be isolated.

Slow neutron irradiation of ^{30}Si has also been used to produce ^{31}Si . The product spectrum from the reactor-neutron irradiation of silane differs from that obtained from the fast-neutron irradiation of phosphine-silane mixtures. Trisilane, a prominent product from the thermal-neutron-induced reaction is absent from the reactions induced by fast neutrons. While the details of reaction mechanism remain to be elucidated, it appears that the differences in the chemistry induced by the two modes of formation of ^{31}Si result from the incursion of ionic species in the slow neutron case. This is indicated by the increase in yields which accompanies the addition of substances with low ionization potentials such as ammonia and phosphine to the reaction mixtures. Product ratios are not changed by the addition of phosphine and ammonia, indicating that the effects of these added substances are on early stages in the reaction sequence.

Experiments have also been carried out on the chemistry of recoiling germanium atoms. Free germanium atoms have been produced by the fast-neutron induced nuclear transformation $^{76}Ge(n,2n)^{75}Ge$. The reactions of germanium atoms with germane

produce $^{75}\text{GeH}_4$ and $\text{H}_3^{75}\text{GeGeH}_3$, quite analogous to the reactions of silicon atoms with silane. When silane is added to the reaction mixture, germylsilane is produced along with germane and digermane. Germane is approximately ten times as reactive toward recoiling germanium atoms than is silane.

Two papers have been submitted for publication this past year. Both have been accepted and are in press:

1. COO-1713-3 "Reactions of Recoiling Silicon Atoms with Phosphine, Silane and Ethylene" by Peter P. Gaspar, S. Allan Bock and William C. Eckelman, J. Am. Chem. Soc., in press.
2. COO-1713-4 "Reactions with Silane of Silicon Atoms Recoiling from $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ " by Peter P. Gaspar, S. Allan Bock and Carl A. Levy, Chemical Communications in press.

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