Reactions of Recoiling Silicon Atoms with Phosphine Silane and Disilane¹**MASTER**

(1) Financial support from the United States Atomic Energy Commission is gratefully acknowledged. This is AEC report No. C00-1713-16.

The formation of disilane $\text{H}_3^{31}\text{SiSiH}_3$ and silane $^{31}\text{SiH}_4$ from the fast-neutron irradiation of phosphine-silane mixtures has been rationalized by proposing a set of product-determining steps involving the intermediate silylene: $^{31}\text{SiH}_2$ which is the product of the primary reactions of recoiling silicon atoms.²

(2) P.P. Gaspar, S.A. Block and W. C. Eckelman, J. Amer. Chem. Soc., **90**, 6914 (1968).

The present report provides support for the intermediacy of $^{31}\text{SiH}_2$ and suggests the occurrence of a novel reaction—the insertion of $^{31}\text{SiH}_2$ into silicon-silicon bonds.

An alternative mechanism for the formation of $\text{H}_3^{31}\text{SiSiH}_3$ involving the coupling of silyl radicals, $^{31}\text{SiH}_3$ with nonradioactive $^{31}\text{SiH}_3$ formed from silane by radiation damage, had been rendered unlikely by the failure of scavengers (NO , C_2H_4) to affect product yields.² However, the reaction

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

efficiencies of the scavengers employed toward silyl radicals is unknown, and further evidence for the intermediacy of $^{31}\text{SiH}_2$ rather than $^{31}\text{SiH}_3$ is desirable. To this end the fast-neutron irradiation of phosphine-disilane mixtures was undertaken, since in this system the insertion of $^{31}\text{SiH}_2$ into Si-H bonds can be distinguished from the coupling of $^{31}\text{SiH}_3$ with the debris from radiation damage.

Radiation damage in the phosphine-disilane system would be expected to produce $^{31}\text{SiH}_3$ as well as $^{31}\text{SiH}_2\text{SiH}_3$,³ and thus coupling with $^{31}\text{SiH}_3$ would lead

(3) While the radiolysis of disilane has not been reported, it is well-known that both C-C and C-H bond-rupture occur in the radiolysis of hydrocarbons. See S.C. Lind, Radiation Chemistry of Gases, Reinhold, N.Y., 1961, pp. 103, 179; also A.V. Topchiev (ed.), Radiolysis of Hydrocarbons, Elsevier, Amsterdam, 1964.

to the formation of significant amounts of $\text{H}_3^{31}\text{SiSiH}_3$ as well as $\text{H}_3^{31}\text{SiSiH}_2\text{SiH}_3$. In the event that $^{31}\text{SiH}_2$ is the predominant intermediate the major expected product is trisilane $^{31}\text{SiSi}_2\text{H}_8$ formed by Si-H insertion.

The results of fast-neutron irradiation of mixtures of phosphine with silane, disilane and both silane and disilane are given in Table I. The product distributions suggest the following conclusions:

1. The small amount of $\text{H}_3^{31}\text{SiSiH}_3$ and the large amount of $^{31}\text{SiSi}_2\text{H}_8$ formed from the reactions of recoiling silicon atoms in phosphine-disilane mixture are in accord with the intermediacy of $^{31}\text{SiH}_2$ which inserts into the Si-H (or Si-Si, vide infra) bonds of disilane to form the major product.

2. The formation of small amounts of $\text{H}_3^{31}\text{SiSiH}_3$ and $^{31}\text{SiH}_4$ from phosphine-disilane mixture suggests a mechanism for the formation of these products, and for the formation of $^{31}\text{SiH}_4$ from phosphine-silane mixtures, consistent with a dominant role for $^{31}\text{SiH}_2$ as reaction intermediate:

Similar thermal decompositions of disilane and trisilane to silylene have been recently suggested to explain the products^{4,5} and reaction kinetics⁵ of disilane and trisilane pyrolysis.

(4) E.N. Tebben and M. A. Ring, Inorg. Chem., 8, 1787 (1969).

(5) M. Bowrey and J.H. Purnell, J. Amer. Chem. Soc., 92, 2594 (1970).

3. The previously overlooked² formation of $^{31}\text{SiSi}_2\text{H}_8$ as a minor product from phosphine-silane mixtures cannot be due to a reaction of $\text{:}^{31}\text{SiH}_2$. The formation of trisilane from silane may be understood, however, if a primordial step toward the production of $\text{:}^{31}\text{SiH}_2$ is the insertion of a silicon atom into an Si-H bond of silane. The resulting divalent species $\text{H-}^{31}\text{Si-siH}_3$ may occasionally survive to take part in a second insertion forming trisilane, although its normal fate seems to be Si-Si bond scission.

4. A remarkably high ratio of $^{31}\text{SiSi}_2\text{H}_8$ to $\text{H}_3^{31}\text{SiSiH}_3$ is obtained from phosphine-silane-disilane mixtures. A reactivity ratio, disilane to silane, of 4.9 ± 1.9 has been obtained from a series of experiments in which the silane-disilane ratio varied from 0.25 to 4.0. Since the ratio of Si-H bonds in the two molecules is 6:4, it is clear that either the Si-H bonds of disilane are considerably more reactive toward insertion by $\text{:}^{31}\text{SiH}_2$ than are the bonds

of silane, or $:^{31}\text{SiH}_2$ is undergoing insertion into the Si-Si bond of disilane to form $\text{H}_3\text{Si}^{31}\text{SiH}_2\text{SiH}_3$ as well as $\text{H}_3^{31}\text{SiSiH}_2\text{SiH}_3$ by Si-H insertion.

It has recently been suggested that the Si-H bonds of disilane may be weaker than those in silane,⁶ and this may explain the differential reactivity toward

(6) R.P. Hollandsworth and M.A. Ring, Inorg. Chem., 7, 1635 (1968).

silylene. On the other hand, Si-Si bond insertion has been noted as a possible explanation for a slightly greater than statistical ratio of n-tetrasilane to iso-tetrasilane believed to have resulted from reaction of $:\text{SiH}_2$ with trisilane.⁵

We are continuing to investigate the possible insertion of $:^{31}\text{SiH}_2$ into Si-Si bonds by appropriate product degradation studies.

Peter P. Gaspar, Peter Markusch

Department of Chemistry

Washington University

Saint Louis, Missouri 63130

Table I.^a Yields of ³¹Si-Labeled Products from Reactions of ³¹Si Atoms

Expt	Substrate	³¹ SiH ₄ ^b	H ₃ ³¹ SiSiH ₃ ^b	³¹ SiSi ₂ H ₈ ^b
A	1:1 PH ₃ : SiH ₄	18,300 ± 2,700	61,100 ± 9,200	8,900 ± 1,300
A	1:1 PH ₃ : SiH ₄	18,300 ± 2,700	67,300 ± 10,100	10,000 ± 1,500
A	1:1 PH ₃ : H ₃ SiSiH ₃	6,800 ± 1,000	4,400 ± 700	58,300 ± 8,700
A	1:1:1 PH ₃ : SiH ₄ : H ₃ SiSiH ₃	7,100 ± 1,100	11,800 ± 1,800	44,400 ± 6,700
A	1:1:1 PH ₃ : SiH ₄ : H ₃ SiSiH ₃	5,700 ± 900	10,600 ± 1,600	47,800 ± 7,200
B	5:1:4 PH ₃ : SiH ₄ : H ₃ SiSiH ₃	7,900 ± 1,200	7,800 ± 1,200	60,700 ± 9,100
B	5:4:1 PH ₃ : SiH ₄ : H ₃ SiSiH ₃	6,400 ± 1,000	26,500 ± 4,000	17,900 ± 2,300

^aAll samples at total pressure 2.0 ± 0.1 atm and, within an experiment, irradiated simultaneously at equal neutron flux as described in ref 2. ^bYields given as counts above background extrapolated to a common time for each experiment to correct for decay. Absolute combined yields of products as % of total ³¹Si produced are 40-60%.