Reactions of Recoiling Silicon Atoms with Phosphine, Silane, and Disilane

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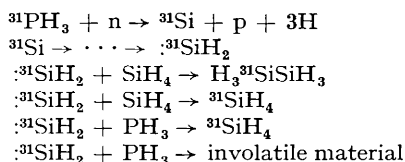
Summary A high ratio of radioactive trisilane to disilane obtained from the reactions of silicon atoms in phosphine–disilane mixtures is evidence for insertion by $:^{31}SiH_2$ as the product-determining step.

THE formation of disilane $H_3{}^{31}SiSiH_3$ and silane $^{31}SiH_4$ from the fast-neutron irradiation of phosphine–silane mixtures has been rationalized on the basis of a set of product-determining steps involving the intermediate silylene $^{31}SH_2$, which is the product of the primary reactions of recoiling silicon atoms.[1]



$$^{31}PH_3 + n \rightarrow {}^{31}Si + p + 3H$$
$$^{31}Si \rightarrow \cdots \rightarrow :^{31}SiH_2$$
$$:^{31}SiH_2 + SiH_4 \rightarrow H_3{}^{31}SiSiH_3$$
$$:^{31}SiH_2 + SiH_4 \rightarrow {}^{31}SiH_4$$
$$:^{31}SiH_2 + PH_3 \rightarrow {}^{31}SiH_4$$
$$:^{31}SiH_2 + PH_3 \rightarrow \text{involatile material}$$

Our recent experiments provide support for the intermediacy of $:^{31}SiH_2$ and suggest the occurrence of a novel reaction, the insertion of $:^{31}SiH_2$ into silicon–silicon bonds.

An alternative mechanism for the formation of $H_3{}^{31}SiSiH_3$ involving the coupling of silyl radicals, $^{31}SiH_3\cdot$ with non-radioactive $SiH_3\cdot$ formed from silane by radiation damage, had been rendered unlikely by the failure of scavengers (NO, C_2H_4) to affect product yields.[1] However, the reaction efficiencies of the scavengers employed towards silyl radicals are unknown, and further evidence for the intermediacy of $:^{31}SiH_2$ rather than $^{31}SiH_3\cdot$ is desirable. The fast-neutron irradiation of phosphine–disilane mixtures was therefore studied, since in this system the insertion of $:^{31}SiH_2$ into Si–H bonds can be distinguished from the coupling of $^{31}SiH_3\cdot$ with the debris from radiation damage.

Radiation damage in the phosphine–disilane system would be expected to produce $SiH_3\cdot$ as well as $SiH_3SiH_2\cdot$,[2] and thus coupling with $^{31}SiH_3\cdot$ would lead to the formation of significant amounts of $H_3{}^{31}SiSiH_3$ as well as $H_3{}^{31}SiSiH_2$-SiH_3. In the event that $:^{31}SiH_2$ is the predominant intermediate the major expected product is trisilane $^{31}SiSi_2H_8$ 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 the Table. The product distributions suggest the following conclusions:

(i) The small amount of $H_3{}^{31}SiSiH_3$ and the large amount of $^{31}SiSi_2H_8$ formed from the reactions of recoiling silicon atoms in phosphine–disilane mixture are in accord with the intermediacy of $:^{31}SiH_2$ which inserts into the Si–H (or Si–Si, *vide infra*) bonds of disilane to form the major product.

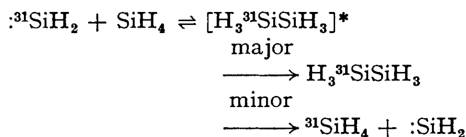
(ii) The formation of small amounts of $H_3{}^{31}SiSiH_3$ *and* $^{31}SiH_4$ from phosphine–disilane mixture suggests a mechanism for the formation of these products, and for the formation of $^{31}SiH_4$ from phosphine–silane mixtures, consistent

Yields of ^{31}Si*-labelled products from reactions of* ^{31}Si *atoms*[a]

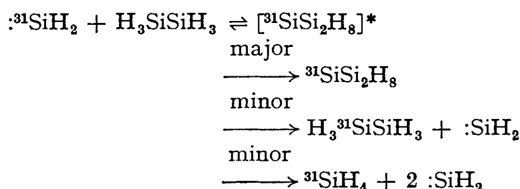
Expt	Substrate	$^{31}SiH_4$[b]	$H_3{}^{31}SiSiH_3$[b]	$^{31}SiSi_2H_8$[b]
A	1:1 $PH_3:SiH_4$	18,300 ± 2700	61,100 ± 9200	8900 ± 1300
A	1:1 $PH_3:SiH_4$	18,300 ± 2700	67,300 ± 10,100	10,000 ± 1500
A	1:1 $PH_3:H_3SiSiH_3$	6800 ± 1000	4400 ± 700	58,300 ± 8700
A	1:1:1 $PH_3:SiH_4:H_3SiSiH_3$	7100 ± 1100	11,800 ± 1800	44,400 ± 6700
A	1:1:1 $PH_3:SiH_4:H_3SiSiH_3$	5700 ± 900	10,600 ± 1600	47,800 ± 7200
B	5:1:4 $PH_3:SiH_4:H_3SiSiH_3$	7900 ± 1200	7800 ± 1200	60,700 ± 9100
B	5:4:1 $PH_3:SiH_4:H_3SiSiH_3$	6400 ± 1000	26,500 ± 4000	17,900 ± 2300

[a] All samples at total pressure 2·0 ± 0·1 atm and, within an experiment, irradiated simultaneously at equal neutron flux as described in ref. 1. [b] Yields 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 ^{31}Si produced are 40—60%.

with a dominant role for $:^{31}SiH_2$ as reaction intermediate:



$$:^{31}SiH_2 + SiH_4 \rightleftharpoons [H_3{}^{31}SiSiH_3]^* \xrightarrow{\text{major}} H_3{}^{31}SiSiH_3 \quad \xrightarrow{\text{minor}} {}^{31}SiH_4 + :SiH_2$$



$$:^{31}SiH_2 + H_3SiSiH_3 \rightleftharpoons [^{31}SiSi_2H_8]^* \xrightarrow{\text{major}} {}^{31}SiSi_2H_8 \quad \xrightarrow{\text{minor}} H_3{}^{31}SiSiH_3 + :SiH_2 \quad \xrightarrow{\text{minor}} {}^{31}SiH_4 + 2\ :SiH_2$$

Similar thermal decompositions of disilane and trisilane to silylene have been recently suggested to explain the products[3,4] and reaction kinetics[4] of disilane and trisilane pyrolysis.

(iii) The previously overlooked[2] formation of $^{31}SiSi_2H_8$ as a minor product from phosphine–silane mixtures cannot be due to a reaction of $:^{31}SiH_2$. The formation of trisilane from silane may be understood, however, if a primordial step toward the production of $:^{31}SiH_2$ is the insertion of a silicon atom into an Si–H bond of silane. The resulting bivalent species H–^{31}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.

(iv) A remarkably high ratio of $^{31}SiSi_2H_8$ to $H_3{}^{31}SiSiH_3$ 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 if 6:4, it is clear that either the Si–H bonds of disilane are considerably more reactive towards insertion by $:^{31}SiH_2$ than are the bonds of silane, or $:^{31}SiH_2$ is undergoing insertion into the Si–Si bond of disilane to form $H_3Si^{31}SiH_2SiH_3$ as well as $H_3{}^{31}Si$-SiH_2SiH_3 by Si–H insertion.

It has recently been suggested that the Si–H bonds of disilane may be weaker than those in silane,[5] and this may explain the differential reactivity towards 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 $:SiH_2$ with trisilane.[4]

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[1] P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Amer. Chem. Soc.*, 1968, **90**, 6914.
[2] 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, New York, 1961, pp. 103, 179; also A. V. Topchiev (ed.), "Radiolysis of Hydrocarbons," Elsevier, Amsterdam, 1964.
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