Reactions of Recoiling Silicon Atoms with Phosphine, Silane, and Ethylene[1]

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Abstract: Fast-neutron irradiation of phosphine produces neutral silicon-31 atoms whose chemically stable end product is $^{31}SiH_4$. Phosphine–silane mixtures yield $H_3{}^{31}SiSiH_3$ and $^{31}SiH_4$, the product ratio increasing rapidly with silane concentration until a plateau value of 4.8 ± 0.9 is reached at *ca.* 20% silane. The absolute yields increase linearly with silane concentration over the range (0–80%) studied. The yield *vs.* composition data are accommodated by a kinetic scheme in which a single species reacts with silane and phosphine to give $^{31}SiH_4$, with silane to give $H_3{}^{31}SiSiH_3$, and with phosphine to give an involatile product. The major product from 1:1 phosphine–ethylene mixtures is tentatively identified as $^{31}SiH_3CH_2CH_2PH_2$. The occurrence of a "hot" process in the reaction sequence is indicated by a large moderator effect on the absolute yields of products from phosphine–silane mixtures.

As a first step toward an exploration of the chemistry of atomic silicon,[2] experiments have been undertaken in which silicon atoms recoiling from a nuclear transformation are produced in gaseous phosphine, phosphine–silane, and phosphine–ethylene mixtures. Our goals in this study are a knowledge of the scope and fundamental mechanisms of silicon atom reactions and an understanding of the roles of electronic structure and kinetic energy as factors determining the reactions of silicon atoms. In this report the dependence of product yields on such parameters as the composition and pressure of the reaction mixture and on the presence of moderator or scavengers is presented. These data have allowed limited conclusions to be reached concerning the mechanisms of product-forming steps. The effect of excess kinetic energy on the reactivity of intermediate silicon species is discussed.

Outline of Technique

In these experiments a small number of radioactive silicon atoms with high kinetic energies is produced by nuclear reaction in the gas phase. The recoiling silicon atoms are born in an environment of normal gas molecules at room temperature. After most of their initial energy is dissipated in collisions, the silicon atoms enter into a series of chemical reactions. The chemically stable end products containing the radioactive silicon atoms are separated and analyzed by a gas chromatograph in series with two proportional flow counters. Conclusions about the reaction sequence which results in the observed stable end products are based on the qualitative and quantitative changes in the products which accompany changes in the reaction conditions. This approach to gas-phase hot-atom chemistry was pioneered by Willard,[3] Rowland,[4] Wolf,[5] and Wolfgang[6] in their studies of the reactions of recoiling halogen, tritium, and carbon atoms.

Atomic silicon (^{31}Si, half-life 2.65 hr[7]) is produced from gaseous phosphine by the nuclear reaction $^{31}P(n,p)^{31}Si$, whose cross section[8] is *ca.* 10^2 mbarns. The nuclear reaction is induced by a flux of *ca.* 10^8 neutrons/(cm^2 sec) produced by the Washington University cyclotron from the transformation $^{9}Be(d,n)^{10}B$, which is *in turn* induced by a 100-μA current of 14-MeV deuterons. The *ca.* 10^7 silicon atoms produced in each experiment are born with a recoil energy of *ca.* 6×10^5 eV,[9] thus ensuring the breakage of all bonds present in the precursor molecule. Initially the recoiling silicon atoms are likely to be positively charged.[10] The energies at which cross sections reach maximum values for the various charge-transfer processes in which silicon atoms can take part have been calculated according to the resonance rule.[11] As seen in Table I, these calculations indicate that processes which lead to the ionization of a silicon atom reach maximum cross sections at *higher* energies than processes which neutralize silicon ions. Therefore silicon atoms with high initial recoil energies (10^5 eV) should reach the energy region of chemical reactions ($<10^2$ eV) as neutral atoms. This conclusion would *not* be warranted for the alternative route to ^{31}Si utilizing a convenient thermal-neutron irradiation $^{30}Si(n,\gamma)^{31}Si$. The n,γ reaction produces silicon atoms with 75- to 750-eV[12] recoil energy. The question whether silicon atoms undergo chemical reactions at high kinetic energies is considered in the discussion of moderator experiments.

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(1) AEC Standard Technical Report No. COO-1713-3.

(2) (a) For a preliminary communication see P. P. Gaspar, B. D. Pate, and W. Eckelman, *J. Am. Chem. Soc.*, **88**, 3878 (1966); (b) P. S. Skell and P. W. Owen, *ibid.*, **89**, 3933 (1967).

(3) J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); J. B. Evans and J. E. Willard, *J. Am. Chem. Soc.*, **78**, 2908 (1956).

(4) E. K. C. Lee, J. W. Root, and F. S. Rowland in "Chemical Effects of Nuclear Transformations," Vol. I, International Atomic Energy Agency, Vienna, 1965, p 55.

(5) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964).

(6) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

(7) C. M. Lederer, J. M. Hollander, and I. Perlman, "Table of Isotopes," 6th ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 10.

(8) J. R. Stehn, M. D. Goldberg, B. A. Magurno, and R. Wiener-Chasman, "Neutron Cross Sections," Brookhaven National Laboratory, Upton, N. Y., 1964, p 15-0-5.

(9) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p 263.

(10) A calculation using the method of B. G. Harvey, *Ann. Rev. Nucl. Sci.*, **10**, 235 (1960), gives an average charge of +2.1.

(11) (a) H. S. Massey and E. H. Burhop, "Electronic and Ionic Impact Phenomena," Clarendon Press, Oxford, 1952, p 441; (b) J. B. Hasted, "Physics of Atomic Collisions," Butterworth & Co. (Publishers) Ltd., London, 1964, p 420. (c) For examples of large charge-transfer cross sections at velocities low compared to maxima predicted by the resonance rule, see G. K. Lavrovskaya, M. I. Markin, and V. L. Tal'roze, *Kinetics Catalysis* (USSR), **2**, 21 (1961).

(12) Recoil energy is 750 eV if the mass excess of ^{31}Si over $^{30}Si + n$ is employed as the maximum γ energy (6.59 MeV). If maximum γ energy is ≤ 2 MeV, recoil energy is ≤ 75 eV.

Table I. Energies at Which Cross Sections Reach Maximum Values as Calculated from the Resonance Rule

	Phosphine		Silane		Ethylene		Neon	
	$\lvert\Delta E\rvert^a$	$E_{max} \times 10^{-5}$ [a,b]	$\lvert\Delta E\rvert$	$E_{max} \times 10^{-5}$	$\lvert\Delta E\rvert$	$E_{max} \times 10^{-5}$	$\lvert\Delta E\rvert$	$E_{max} \times 10^{-5}$
$Si(^3P) + M = Si^+ + M + e^-$	8.12	2.9	3.12	2.9	8.12	2.9	8.12	2.9
$Si(^1D) + M = Si^+ + M + e^-$	7.37	2.5	7.37	2.5	7.37	2.5	7.37	2.5
$Si^+ + M = Si(^3P) + M^+$	1.88	0.16	4.08	0.77	2.44	0.27	13.44	8.4
$Si^+ + M = Si(^1D) + M^+$	2.63	0.12	4.83	0.22	3.19	0.15	14.19	9.3
$Si(^1D) + M = Si(^3P) + M$	0.75	0.026	0.75	0.026	0.75	0.026	0.75	0.026
$Si(^1D) + M = Si(^3P) + M^*$	...	...	...	...	3.85	0.68	...	...
$Si(^3P) + M = Si(^1D) + M^*$	...	...	...	...	5.35	1.30	...	...

[a] $E_{max} = 0.5m[a\Delta E/h]^2 = 4630[\Delta E]^2$ for ΔE in eV; E_{max} in eV;[11] a = 7 A. [b] Ionization potentials (eV): $Si(^3P)$ 8.12 and $Si(^1D)$ 7.37 (G. Herzberg "Atomic Spectra and Atomic Structure," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1937, p 140); PH_3 10.0, SiH_4 12.2, C_2H_4 10.56, and Ne 21.56: (F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 243 ff); $C_2H_4 = C_2H_4(T)$ 4.6 (R. S. Mulliken, *J. Chem. Phys.*, **33**, 1596 (1960)).

Experimental Section

Materials. Phosphine (99.5%) was obtained from the Rocky Mountain Research Co. and used without purification. No impurities could be detected by vapor chromatography. No phosphorus–chlorine bonds were detected by infrared spectroscopy. Silane and disilane were synthesized by lithium aluminum hydride reduction of silicon tetrachloride and hexachlorodisilane,[13] and purified by bulb-to-bulb distillation in a vacuum system. Silane (99.5%) was also purchased from Matheson Co. and used without further purification. Phosphine, silane, and disilane were stored in Pyrex bulbs fitted with vacuum stopcocks. Methane (99.5%), ethane (99.0%), ethylene (99.0%), nitric oxide (98.5%), and carbon tetrafluoride (95.0%) were obtained from Matheson Co. and used without purification. Silylphosphine was produced by heating a mixture of phosphine and silane in a sealed ampoule at 440° for 15 min.[14] A number of organosilicon compounds were required as reference compounds for the calibration of vapor chromatographic columns. Those not purchased were synthesized by standard methods and identified by comparison of physical properties (boiling points, infrared and nuclear magnetic resonance spectra) with those given in the literature. Table II lists these compounds with their sources and syntheses in order of ascending boiling points.

Table II. Sources and Syntheses of Organosilicon Compounds

Compound	Source or synthesis	Ref
CH_3SiH_3	Pierce Chemical Co.	...
$HC\equiv CSiH_3$	Addition of $NaC\equiv CH$ to $SiCl_4$ followed by lithium aluminum hydride (LAH) reduction	...
$H_2C{=}CHSiH_3$	LAH reduction of $H_2C{=}CHSiCl_3$	13
$(CH_3)_2SiH_2$	Pierce Chemical Co.	...
$CH_3CH_2SiH_3$	LAH reduction of $CH_3CH_2SiCl_3$	13
$(CH_3)_3SiH$	Pierce Chemical Co.	...
$(H_2C{=}CH)_2SiH_2$	Addition of $H_2C{=}CHMgBr$ to $H_2C{=}CHSiCl_3$ followed by LAH reduction	*a*
$H_2C{=}CHSiH_2CH_2CH_3$	Addition of CH_3CH_2MgBr to $H_2C{=}CHSiCl_3$ followed by LAH reduction	*a*
$(CH_3)_4Si$	Pierce Chemical Co.	...
$H_2C{=}CHCH_2CH_2SiH_3$	Addition of $H_2C{=}CHCH_2CH_2MgBr$ to $SiCl_4$ followed by LAH reduction	*a*
$CH_3CH{=}CHCH_2SiH_3$	Pt-catalyzed addition of $HSiCl_3$ to butadiene followed by LAH reduction	*b*
$(CH_2)_4SiH_2$	Pt-catalyzed addition of $HSiCl_3$ to $H_2C{=}CHCH_2CH_2Br$ followed by cyclization with Mg and LAH reduction; also by addition of $SiCl_4$ to $BrMg(CH_2)_4MgBr$ followed by LAH reduction	*b, c*
$(CH_3CH_2)_3SiH$	Pierce Chemical Co.	...

[a] R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964). [b] J. Laane, *ibid.*, **89**, 1144 (1967); D. L. Bailey and A. N. Pines, *Ind. Eng. Chem.*, **46**, 2363 (1954). [c] R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

Reaction Mixtures. All neutron irradiations are carried out in sealed quartz ampoules 6 mm i.d. × 9 cm. Unless otherwise specified, the total pressure of the reaction mixtures is 2.2 ± 0.1 atm. Under these conditions the range of a recoiling ^{31}Si atom is *ca.* 1.75 mm; thus <16% of the recoiling atoms could reach a wall. Reaction mixtures are prepared on a conventional high-vacuum line. During neutron irradiations, usually of 30-min duration, the ampoules irradiated together are strapped to a polyethylene spindle and rotated at low speed in order to ensure equal flux for all of the reaction mixtures.

Analysis of Reaction Mixtures. A schematic diagram of the analytical system is shown in Figure 1. The apparatus consists of a homemade conventional vapor chromatograph in series with two gas flow proportional counters. This is a two-counter version of the apparatus described by Wolfgang and Rowland.[15] A reaction mixture is introduced into the chromatograph by crushing the ampoule in which the reaction took place in a previously evacuated and then helium-purged inlet manifold. The sample breaking chamber consists of a 4-in. section of thick-walled Tygon tubing. Ampoules are broken by compression with an ordinary C clamp. Several ampoules can be broken together, permitting introduction of carriers. The first flow counter monitors total volatile radioactivity in the reaction mixture, while the second counter monitors the radioactivity contained in the fractions eluted from the chromatographic

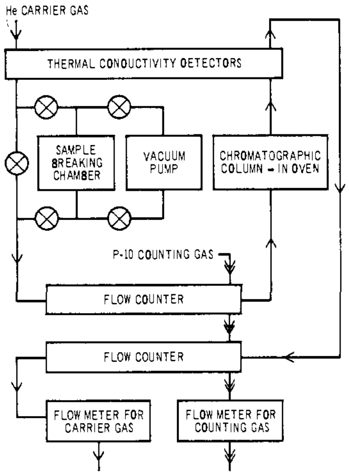

Figure 1. Schematic diagram of analytical system.

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(13) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

(14) G. Fritz, *Fortschr. Chem. Forsch.*, **4**, 459 (1963).

(15) (a) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958); (b) J. K. Lee, E. K. C. Lee, B. Musgrave, Y. Tang, J. W. Root, and F. S. Rowland, *ibid.*, **34**, 741 (1962).

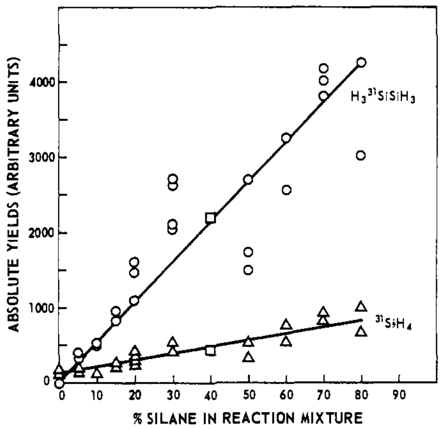

Figure 2. Variation of absolute product yields from phosphine–silane mixtures with composition at constant total pressure (2.2 ± 0.1 atm). Squares indicate reaction points assumed constant among different runs to correct for flux differences. Arbitrary units can be converted to percentage units using observed value 44 ± 16% for yield of $^{31}SiH_4$ + $H_3{}^{31}SiSiH_3$ from 50% silane mixtures.

column as they emerge. Reaction products are identified by comparison of retention times (with those of authentic samples) on several chromatographic columns differing in stationary phase and separatory characteristics. Simultaneous measurement of the thermal conductivity and radioactivity of the effluent gas stream gives retention times for both the macroscopic components of the reaction mixtures (silicon precursor, reaction substrates, scavengers, moderators, product carriers) and the microscopic quantities of radioactive products.

The counters are the sandwich-type window vapor-flow proportional counter described by Wolfgang.[16] The relative efficiencies of the two counters under the conditions used to analyze reaction mixtures are determined by passing radioactive samples (^{41}Ar), which are known to be unattenuated by the chromatographic system, through both counters and comparing the total counts recorded by the two counters. The ratio of the counting efficiency of the first counter to that of the second counter varies from 1.6 to 2.4. The relative efficiency is a function of flow rate and pressure drop between the two counters.

The chromatographic columns are constructed of 0.25-in. diameter aluminum or stainless steel. The inlet manifold, detector block, and connecting tubing are of stainless steel. Stationary phases (except Porapak) are supported on 40–50 mesh diatomaceous earth (Anakrom ABS, acid- and base-washed and silanized). Stationary phase lengths and compositions (weight per 100 g of Anakrom) are as follows: 40-ft 2,4-dimethylsulfolane, 30%; 18-ft diethyl phthalate, 60%, plus DC710 silicone oil, 20%; 30-ft SF-96 silicone oil, 20%; and 12-ft Porapak Q (50–80 mesh).

Dose. The total dose in these experiments was less than 10^{-2} eV per molecule, as determined by acetylene dosimetry.[17] With a dose of 3.08 × 10^{-2} eV/molecule, Ando[18] obtained 0.1% Si_2H_6 and 0.4% H_2 on irradiation of silane at atmospheric pressure with a ^{60}Co source. It is therefore believed that radiation damage is not significant in the present experiments.

Absolute Yield Measurements. Absolute yields of products obtained in simultaneous irradiations could be *compared* by presenting the yields in arbitrary units of counts per radioactive "peak" divided by the amount of phosphine in the particular sample. Neutron fluxes and analytical conditions were constant for a set of experiments. True absolute yields were obtained by trapping a radioactive product on activated charcoal and comparing the induced activity (measured in a 2π geometry proportional counter) with that induced in a solid standard red phosphorus sample irradiated simultaneously with the reaction mixture. The absolute yield is the ratio of the activities corrected for the differing masses of phosphorus in the standard and the reaction mixture.

Errors. The data are subject to the following sources of error. Sample volumes are uncertain by ±3%, sample pressures by ±5%, and peak areas in vapor chromatograms by ±5%. Losses of carrier-free radioactive products in the analytical system as great as 20% have been encountered. Variation in gas flow rate during the elution of a macroscopic "peak" from the vapor chromatograph (variation due to gas stream inhomogeneity) has been found by Wolf and Welch to produce an error of 15% in the estimation of the radioactivity flowing through a counter.[19] Uncertainties in radioactive peak boundaries in the chromatograms could result in errors as large as ±10%. Statistical variation of radioactive decay leads to only a small uncertainty in our results, ±5% for a peak containing 500 counts above background, but only 1.5% for a peak of 5000 counts.

The reproducibility of the data indicates that the actual uncertainties are moderate. Fifteen independent determinations of the relative yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ from 1:1 PH_3–SiH_4 mixtures gave results with a standard deviation of ±2.7%. In these experiments, ratios of individual product activities were determined. The standard deviation for ten independent determinations of the recovery of volatile radioactivity in the same experiments was ±16%. Here ratios of individual product activities to total volatile radioactivity were measured. These standard deviations in duplicate experiments were assigned as probable errors to data collected under similar conditions for which no duplicate experiments were available. Ratios of product activities, ratios of product activities to the total volatile radioactivity produced in a sample, and absolute product activities were all assigned probable errors of ±16%.

Hazardous Procedures. Phosphine, silane, and disilane were handled routinely in a vacuum line which could be evacuated to 10^{-5} mm with a diffusion pump. When oxygen was accidentally admitted to the apparatus, violent explosions occurred. Silane burns at a concentration of oxygen tolerated by phosphine and disilane burns at an oxygen concentration tolerated by silane.

Results

The following reaction mixtures have been subjected to fast-neutron irradiation: (a) pure phosphine, (b) phosphine–silane mixtures, (c) phosphine–silane mixtures containing small amounts of scavengers, (d) phosphine–ethylene mixtures, (e) phosphine–ethylene mixtures containing small amounts of silane, and (f) phosphine–silane–neon mixtures.

Phosphine. Pure phosphine has been irradiated with fast neutrons in order to determine the products of reaction between recoiling silicon atoms and phosphine. The only radioactive product eluted from a variety of chromatographic columns is silane, $^{31}SiH_4$, obtained in erratic yields ranging from 67 to 100% of the total volatile activity in the reaction mixture. The absolute yield of $^{31}SiH_4$ is only *ca.* 2% of the total ^{31}Si produced. The variation in yield is due in part to losses incurred during analysis, as is shown by an increase in yield when silane carrier is added *after* irradiation.

Phosphine–Silane Mixtures. Addition of nonradioactive silane to reaction mixtures *prior* to neutron irradiation results in an increase in the absolute yield of $^{31}SiH_4$ and the formation of a new radioactive product, disilane, $H_3{}^{31}SiSiH_3$. A comparison of absolute yields at various silane concentrations is given in Table III and Figure 2. Within experimental error (±16%) the entire volatile radioactivity consists of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$, which account for 44% of the total ^{31}Si produced at a 1:1 phosphine:silane ratio. No radioactive trisilane is observed among the products under conditions where 1% would be detected.[20]

The variation of the relative yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ as functions of the nonradioactive silane concentration is given in Figure 3. The relative yields

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(16) R. Wolfgang and C. MacKay, *Nucleonics*, **16** (10), 69 (1958).

(17) L. M. Dorfman and F. J. Shipko, *J. Am. Chem. Soc.*, 77, 4723 (1955).

(18) W. Ando and S. Oae, *Bull. Chem. Soc. Japan*, **35**, 1540 (1962).

(19) A. P. Wolf and M. Welch, private communication. In the present experiments a much smaller error is expected since sample sizes (2 cc) are much smaller than those of Wolf and Welch (15 cc).

(20) P. P. Gaspar, S. A. Bock, and C. Levy, unpublished results.

Table III. Product Yields from Fast-Neutron Irradiation of Phosphine–Silane Mixtures[a]

PH_3/SiH_4	Total volatile activity (TVA)	TVA/PH_3	$^{31}SiH_4$	$^{31}SiH_4/PH_3$	$H_3{}^{31}SiSiH_3$	$H_3{}^{31}SiSiH_3/PH_3$	($^{31}SiH_4$+ $H_3{}^{31}$-$SiSiH_3$)/TVA
3.21 ± 0.23	29,600 ± 4700[b]	490 ± 80[c]	4200 ± 700[b]	68 ± 12[c]	18,000 ± 2900[b]	290 ± 50[c]	0.97 ± 0.16
4.32 ± 0.30	41,000 ± 6600	560 ± 100	5200 ± 800	72 ± 12	21,700 ± 3500	300 ± 50	0.85 ± 0.14
11.2 ± 0.8	14,500 ± 2300	200 ± 30	3000 ± 500	42 ± 7	8,000 ± 1300	110 ± 20	0.99 ± 0.16
13.8 ± 1.0	16,000 ± 2600	230 ± 40	4600 ± 700	67 ± 11	9,200 ± 1500	130 ± 20	1.12 ± 0.18
∞	3,000 ± 500	50 ± 8	1700 ± 300	27 ± 4	. . .[d]	. . .[d]	0.72 ± 0.12

[a] Samples were irradiated simultaneously at equal neutron flux and contained equal total pressures of 2.2 ± 0.1 atm. [b] Yields are given as counts above background extrapolated to a common time to correct for decay. [c] Absolute yields in arbitrary units of counts per % pen deflection for PH_3 peak in chromatographic thermal conductivity trace. [d] Product sought for and not observed. The limit of detectability under these conditions is *ca.* 200 counts above background.

change rapidly at low silane concentrations but level off to plateau values.

Experiments at different total pressures indicate that the scatter of points in Figures 2 and 3 is *not* due to uncertainties in the total pressure. The variation of relative yields is small between 0.9 and 2.3 atm, as shown in Figure 4.

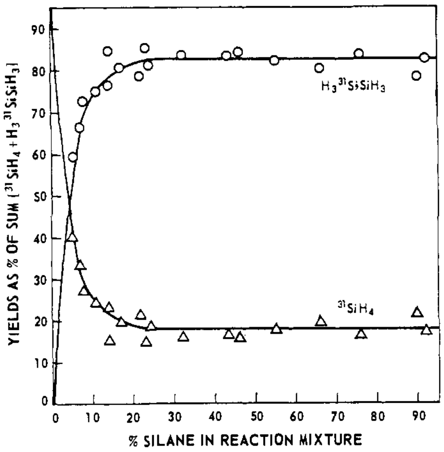

Figure 3. Variation of relative product yields from phosphine–silane mixtures with composition at constant total pressure (2.2 ± 0.1 atm).

Phosphine–Silane Mixtures Containing Small Amounts of Scavengers. In the hope that their reactivity toward recoiling silicon species is sufficiently high to enable them to act as scavengers, and thus aid in the identification of reaction intermediates, small quantities of tetrafluoromethane, ethylene, nitric oxide, and hydrogen have been added to phosphine–silane mixtures prior to neutron irradiation. The results of these scavenger experiments are given in Table IV. Neither the absolute nor the relative yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ are significantly perturbed by the presence of small quantities of these added substances. Methane and ethane are also ineffective as scavengers and function as moderators when present in high concentrations. No new radioactive products are detected in the scavenger experiments.

Phosphine–Ethylene Mixtures. Six radioactive products are detected when 1:1 phosphine–ethylene mixtures are irradiated with fast neutrons. These products comprise more than 80% of the total volatile radioactivity but only account for *ca.* 7% of the total ^{31}Si produced. The yields and chromatographic characteristics of the products are given in Table V.

The two most volatile products have been identified as $^{31}SiH_4$ and $^{31}SiH_3CH_2CH_3$ by comparison of retention times with authentic samples. Radioactive decay analysis of separated fractions trapped from the chromatographic effluent establishes ^{31}Si as sole radionuclide in the six radioactive products from the phosphine–ethylene system. The measured half-life agrees in each case with the literature value[7] within 0.02 hr.

Table IV. Effect of Scavengers on Product Yields from Fast-Neutron Irradiation of 1:1 Phosphine–Silane Mixtures[a]

Expt	Scavenger	Total volatile act. per unit of precursor	$H_3{}^{31}SiSiH_3$/ $^{31}SiH_4$
1[b]	None	300 ± 50[c]	4.4 ± 0.8
1	None	340 ± 60	5.2 ± 1.0
1	4% C_2H_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_2H_4	2200 ± 400	5.2 ± 1.0
2	4% C_2H_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

[a] All samples contained equal total pressures of 2.2 ± 0.1 atm. [b] Within a single experiment all samples were irradiated simultaneously at equal neutron flux. [c] Absolute yields are given in arbitrary units of counts per % pen deflection for PH_3 peaks in chromatographic thermal conductivity trace. Numbers only comparable within single experiments, since neutron flux and chromatograph sensitivity varied from experiment to experiment. [d] Samples irradiated with unequal neutron fluxes. Absolute yields of volatile radioactive products were *not* depressed by these scavengers.

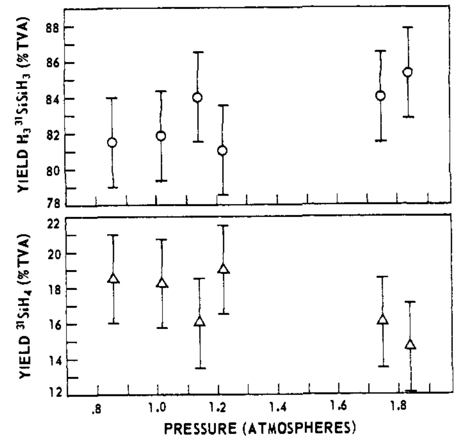

Figure 4. Variation of product yields from phosphine–silane mixtures with total pressure at constant composition (1:1).

Table V. Yields and Vapor Chromatographic Retention Times for Products of Fast-Neutron Irradiations of Phosphine–Ethylene Mixtures, and a Comparison with Authentic Materials

Radioactive products	Yields	Diethyl phthalate–silicon oil[a]	SF-96[a]	Dimethylsulfolane[a]	Porapak Q[a]
$^{31}SiH_4$	22 ± 2[b,c] 5 ± 1[d]	5.5[e,f]	7.5	5.5	1.8
$CH_3CH_2{}^{31}SiH_3$	8 ± 1	7	12	6.5	21.5
#3 (unknown)	<2	. . .	19	8.5	36
#4 (unknown)	9 ± 1	14	37	19.0	50
#5 major product	48 ± 8	27	48	28.0	. . .
#6 (unknown)	7 ± 1	32	. . .	41.5	. . .
Authentic materials					
SiH_4	. . .	4.5	6.5	5.5	. . .
$CH_3CH_2SiH_3$	. . .	6.5	10.5	7	21.5
$(CH_2{=}CH)_2SiH_2$	. . .	15	30	9	. . .
$CH_2{=}CHSiH_2CH_2CH_3$	. . .	15	36.5	. . .	. . .
$CH_2{=}CHCH_2CH_2SiH_3$	. . .	15	39	. . .	. . .
$CH_3CH_2CH_2CH_2SiH_3$	. . .	18	42.5	13.5	. . .
$(CH_3CH_2)_2SiH_2$	. . .	18	45	13.5	. . .
$(CH_2)_4SiH_2$	. . .	33.5	68.5	. . .	. . .

[a] The chromatographic columns are described in the Experimental Section. Flow rates and temperatures are as follows: diethyl phthalate–silicone oil, 45 ml/min at 65°; SF-96, 14 ml/min at 25°; dimethylsulfolane, 54 ml/min at 25°; Porapak Q, 80 ml/min at 25–100°. [b] Yields in % of total volatile radioactivity. The total volatile radioactivity comprises 7 ± 3% of the ^{31}Si produced. Reaction mixtures contained 1:1 PH_3–C_2H_4 at total pressure 2.2 ± 0.1 atm. [c] Yield in absence of carrier. [d] Yield in presence of various carriers added after irradiation. [e] Retention times in minutes. [f] There is a *ca.* 15-sec lag between the thermal conductivity detector and the flow-counter.

Table VI. Dependence of Major Product Yields on Phosphine–Ethylene Ratio and on Precursor[a]

Expt[b]	Reactant ratio		Yields[c]		
			$^{31}SiH_4$	$CH_3CH_2{}^{31}SiH_3$	#5 major product
1	PH_3:C_2H_4	0.33	100 ± 20	100 ± 20	3600 ± 600
1	PH_3:C_2H_4	1.0	360 ± 60	580 ± 90	4600 ± 700
1	PH_3:C_2H_4	3.0	1400 ± 200	790 ± 130	4700 ± 800
1	PH_3:C_2H_4	7.0	2400 ± 400	<50[d]	<100[d]
1	PH_3:C_2H_4	∞	1700 ± 300	<50[d]	<100[d]
2	$(CH_3)_3P$:C_2H_4	1.0	<50[d]	1000 ± 160	<50[d]
2	PH_3:C_2H_4	1.0	170 ± 30	220 ± 30	1700 ± 300

[a] All samples contained equal total pressures of 2.2 ± 0.1 atm. [b] Within a single experiment all samples were irradiated simultaneously at equal neutron flux. [c] Yields are given as counts above background extrapolated to a common time to correct for decay. Yields are also corrected for the varying amount of PH_3 in the reaction mixtures. [d] Product sought for and not observed. Limit of detectability given.

There seem to be no surface effects in this reaction system. Filling the reaction ampoules with glass helices does not affect the product distribution or the yields.

The chromatographic data of Table V suggest that the major product from the phosphine–ethylene system could be an alkyl- or alkenylsilane with empirical formula SiC_4H_n. The accessible SiC_4H_n compounds, divinylsilane, vinylethylsilane, 2- and 3-butenylsilane, diethylsilane, butylsilane, and silacyclopentane, have been compared chromatographically with the major product, and differ from it, as shown in Table V.

Evidence that the major product from the phosphine–ethylene system contains a phosphine moiety is given in Table VI. The yield of the major product passes through a maximum as a function of the phosphine–ethylene ratio. The product is absent when phosphine is replaced by trimethylphosphine as the silicon precursor.

Phosphine–Ethylene Mixtures Containing Small Amounts of Silane. Competition between silane and ethylene for one or more common intermediates has been demonstrated. Various amounts of nonradioactive silane have been added to 1:1 phosphine–ethylene mixtures prior to neutron irradiation. The results shown in Figure 5 indicate that the yield of the major product in the absence of silane decreases with increasing silane concentration, and the yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ increase.

The total volatile radioactivity produced in pure phosphine, phosphine–ethylene, and phosphine–silane mixtures are compared in Table VII.

Table VII. Variation of Total Yield of Volatile Radioactive Products with Change in Reaction System

Expt[a]	Reaction system	Total yield of volatile radioactivity[b]
1	PH_3	1,300 ± 200
1	1:1 PH_3–C_2H_4	2,600 ± 400
1	1:1 PH_3–SiH_4	16,300 ± 2600
2	1:1 PH_3–C_2H_4	5,000 ± 800
2	1:1 PH_3–SiH_4	41,900 ± 6700
3	PH_3	2,600 ± 400
3	1:1 PH_3–SiH_4	25,300 ± 4100

[a] Within a single experiment all samples were irradiated simultaneously at equal neutron flux. All samples contained equal total pressures of 2.2 ± 0.1 atm. [b] Yields are given as counts above background extrapolated to a common time to correct for decay and corrected for varying amounts of phosphine in the reaction mixtures.

Phosphine–Silane–Neon Mixtures. Moderator experiments have been carried out in an attempt to assess

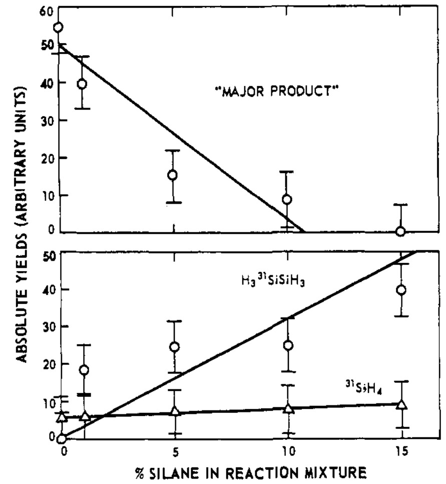

Figure 5. Variation of absolute product yields from phosphine–silane–ethylene mixtures (1:1 PH_3–C_2H_4) with composition at constant total pressure (2.2 ± 0.1 atm). Absolute yield of major product in absence of silane is 7 ± 3 %.

the importance of "hot" reactions in the processes which lead to the observed products. The ratio of neon to a 1:1 phosphine–silane mixture has been varied in a series of experiments at constant total pressure. In a second series at varying total pressure, various amounts of neon have been added to constant amounts of a 1:1 phosphine–silane mixture. The absolute yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ decrease significantly with increasing neon concentration (Figure 6). The relative product yields change by a factor of 2 (Figure 7).

Discussion

Qualitative Conclusions from the Phosphine–Silane System. A low absolute yield (*ca.* 2%) of a single volatile radioactive product, $^{31}SiH_4$, is obtained from the fast-neutron irradiation of pure phosphine. When a few per cent of nonradioactive silane is present in the reaction mixture, there is a fivefold increase in the total yield of the *two* volatile radioactive products, $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ (Table III). The absolute yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ increase with increasing concentration of nonradioactive silane in the reaction mixture (Figure 2). The dramatic effect of nonradioactive silane on relative product yields (Figure 3) is saturated in the concentration region above 20% where constant product ratios ($H_3{}^{31}SiSiH_3/{}^{31}SiH_4 = 4.8 \pm 0.9$) are obtained. These observations indicate that reactions of recoiling silicon species which lead to the formation of volatile products are much more efficient with silane than with phosphine. Thus, reactions of phosphine leading to $^{31}SiH_4$ are negligible at high silane concentrations.

The nearly linear increase in the absolute yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ with increasing concentration of nonradioactive silane suggests that there is a competition for one or more recoiling silicon species between an efficient reaction with silane which produces $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ (*ca.* 80% combined yield at 80% nonradioactive silane) and processes which produce an involatile product. It does not appear that the yields of $H_3{}^{31}SiSiH_3$ and $^{31}SiH_4$ approach an upper limit asymptotically. Therefore the process which produces an involatile product is probably a reaction of phosphine with an efficiency similar to that of the reactions of silane which produce $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$.

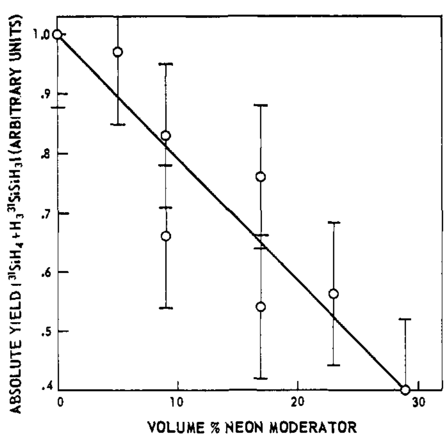

Figure 6. Variation of absolute yields (in arbitrary units) of volatile radioactive products with addition of neon moderator to 1:1 phosphine–silane mixtures (amounts of phosphine and silane held constant, total pressure varying).

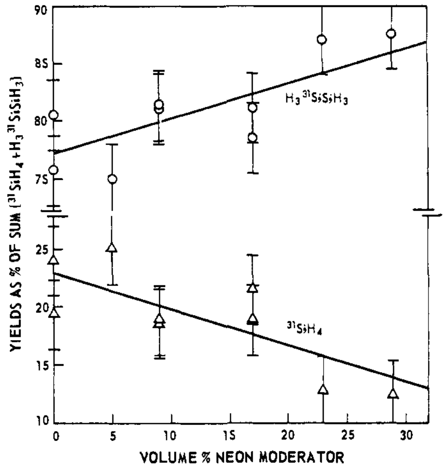

Figure 7. Variation of relative product yields with addition of neon moderator to 1:1 phosphine–silane mixtures (amounts of phosphine and silane held constant, total pressure varying).

Quantitative Conclusions Based on a Kinetic Scheme for the Phosphine–Silane System. While details of reaction mechanism are not yet accessible, it is useful to demonstrate that the available data may be quantitatively analyzed within a simple model. The variation of the absolute (Figure 2) and relative (Figure 3) yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ as functions of the nonradioactive silane concentration can be accommodated by a kinetic scheme involving the reactions of a single intermediate in the product-determining steps[21]

$$X + SiH_4 \xrightarrow{\sigma_1} H_3{}^{31}SiSiH_3$$

$$X + SiH_4 \xrightarrow{\sigma_2} {}^{31}SiH_4$$

$$X + PH_3 \xrightarrow{\sigma_3} {}^{31}SiH_4$$

$$X + PH_3 \xrightarrow{\sigma_4} \text{involatile material}$$

$$\frac{1}{[H_3{}^{31}SiSiH_3]_{abs}} = \frac{\sigma_1 + \sigma_2}{\sigma_1} + \frac{\sigma_3 + \sigma_4}{\sigma_1}\frac{[PH_3]}{[SiH_4]}$$

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(21) The phrase "product determining" avoids deciding the question whether the step is an elementary process which produces the product molecule specified, or instead is the first step in a branch of the mechanism which leads to the product indicated. Reaction cross sections, σ, are used, recognizing the possible variation of reactivity with reactant energy.

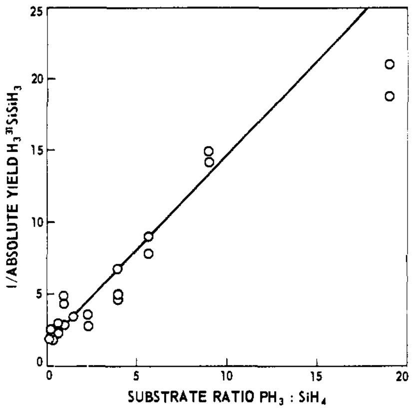

Figure 8. Variation of reciprocal of absolute yield of $H_3{}^{31}SiSiH_3$ from phosphine–silane mixtures with reactant ratio.

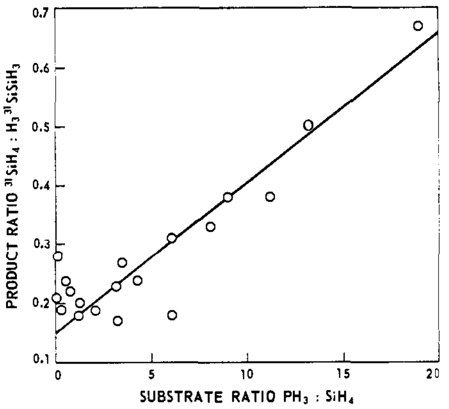

Figure 9. Variation of product ratio from phosphine–silane mixtures with reactant ratio.

where $[H_3{}^{31}SiSiH_3]_{abs}$ is the absolute yield and

$$\frac{[^{31}SiH_4]}{[H_3{}^{31}SiSiH_3]} = \frac{\sigma_2}{\sigma_1} + \frac{\sigma_3[PH_3]}{\sigma_1[SiH_4]}$$

Further

$$[H_3{}^{31}SiSiH_3]_{abs} = \frac{\sigma_1[SiH_4]}{(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)[SiH_4] + \sigma_3 + \sigma_4}$$

where $[H_3{}^{31}SiSiH_3]_{abs}$ is for concentrations expressed as mole fractions; *i.e.*, $[PH_3] = 1 - [SiH_4]$.

According to this analysis, the product ratio, $[^{31}SiH_4]/[H_3{}^{31}SiSiH_3]$, and the reciprocal of the radioactive disilane yield should both be linear functions of the phosphine–silane ratio in the reaction mixtures. The absolute yield of $H_3{}^{31}SiSiH_3$ can also be a linear function of the nonradioactive silane concentration, as observed, if $(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)[SiH_4] \ll (\sigma_3 + \sigma_4)$.

Linear functions are obtained when the data of Figures 2 and 3 are replotted according to these relationships. These are shown in Figures 8 and 9. A ratio of reaction cross sections, $\sigma_1:\sigma_2:\sigma_3 = 1:0.17 \pm 0.04:0.022 \pm 0.005$, is obtained from the slope and intercept of the line fitted by a least-squares analysis to the data of Figure 9. This is to be compared with the value for $\sigma_2/\sigma_1 = 0.42 \pm 0.32$ obtained from the intercept of the line fitted by a least-squares method to the data of Figure 8. From the slope of the line fitted to the data of Figure 8, and the value of σ_3/σ_1 from the data of Figure 9, a value of 1.29 ± 0.48 is obtained for σ_4/σ_1.

It is obvious that a large number of alternative, albeit more elaborate, kinetic schemes can be written which produce the same linear relationships.[22] The kinetic scheme as written is incomplete since it includes only product-determining steps. If the species X is not a silicon atom or if any of the steps written is not an elementary process, then more steps are required. It is indeed possible that the mechanism of this reaction is indeterminate in a formal kinetic sense because there might be more elementary reactions than there are observed products. This would be in accord with the "kinetic uncertainty principle" of Johnson and Cramarossa.[23]

The kinetic scheme includes a single reactive intermediate X, with a single reaction cross section for each of its reactions. Since complete saturation of the valence of a recoiling silicon atom in a single reactive collision is unlikely, several discrete intermediates may be expected to precede the observed products. That the mechanism presented is not wholly adequate for the accommodation of the existing data may be deduced from the deviations from linearity seen at *low* $PH_3:SiH_4$ ratios in Figure 9 and at *high* $PH_3:SiH_4$ ratios in Figure 8. Modification of the kinetic scheme could introduce additional steps with more reactive intermediates, or introduce an effective variation of reaction cross sections with reactant ratio by including varying contributions from hot and thermal processes.

The near-linearity of the absolute yield *vs.* substrate ratio curves for $H_3{}^{31}SiSiH_3$ and $^{31}SiH_4$ indicates that the volatile products are mostly formed in reactions whose efficiencies do not vary with the phosphine–silane ratio. This implies either that all of the reactions of silicon atoms which give volatile products occur at comparable energies (*i.e.*, all reactions are "hot" or all are "thermal") or that the relative reactivity of silicon atoms toward silane and phosphine is not energy dependent.

Indications of "Hot" Reaction from a Moderator Experiment. Experiments with added neon indicate that a "hot" process does occur. Addition of neon to 1:1 phosphine–silane mixtures prior to neutron irradiation causes a significant decrease in the absolute yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ and an increase in the ratio of $H_3{}^{31}SiSiH_3$ to $^{31}SiH_4$. This indicates a reduction of the number of collisions of an excited silicon species with a reactive substrate in the energy range of "hot reactions" by energy loss through nonreactive collisions with inert moderator. Although the ionization potential of neon is sufficiently high to allow the persistence of silicon ions in the energy range of chemical reactions, neon was present in such small concentrations in these experiments that neutralization of silicon ions is to be expected.[24] Even at the highest concentration of neon used (35%), it is not believed that silicon ions intervene in the chemical processes

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[22] A slightly more elaborate mechanism was suggested by an earlier referee; see ref 2a, footnote 17.

[23] H. S. Johnson and F. Cramarossa, *Advan. Photochem.*, 4, 1 (1966). The principle stated concisely is "In a kinetic or photochemical system involving three or more free-radical intermediates, one can never deduce the mechanism by any method which merely analyzes for all the final products and the reactants."

[24] Reference 6, p 109.

which lead to the observed products. Kinetic energy moderation may not be the only process operating, since the effect of added neon is so great.

It is not feasible to decide between two interpretations of this moderator experiment. The first is that there is a "hot" reaction involving an excited precursor to the intermediate X in the product-determining steps of the kinetic scheme. Thus the effect of the moderator is to deactivate a precursor to X and thus remove it from the reaction sequence. The second interpretation of the moderator experiment is that the reactive silicon species in the product-determining steps, X itself, reacts in an excited state. Then the role of the moderator is to deactivate X and remove it from the reaction sequence. Whether or not the kinetic scheme presented includes "hot" or "thermal" reactions depends on which interpretation of the moderator experiment proves to be correct.

While it is obvious that silicon atoms play some role in the reactions which lead to $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$, the identity of other reactive intermediates is of interest. ^{31}SiH, $^{31}SiH_2$, and $^{31}SiH_3$ must all be considered, as well as ^{31}Si. Any of these species may play the role of X in the kinetic scheme, or be otherwise involved in the reaction sequence. Many reactions can be written yielding the observed products from these intermediates, but there is insufficient evidence at this time to make a choice among various plausible alternatives.

Attempts to Identify Reaction Intermediates. Experiments have been carried out in which small amounts of additional substances were added to 1:1 phosphine–silane mixtures before neutron irradiation. It was hoped that the additional substances would prove to be more reactive than silane or phosphine toward the intermediates and thus scavenge them. Scavengers have previously been employed in studies on the thermal and photolytic decomposition of silane.

In photochemical experiments Gunning[25] has found that the presence of 6% nitric oxide completely suppresses the formation of disilane from silane. The mercury-sensitized photodecomposition of silane in a 1:2 silane–ethylene mixture[25] yields a product mixture which consists "principally of ethylsilane." White and Rochow[26] have reported that direct photolysis and pyrolysis of silane in the presence of ethylene also give ethylsilane as a major product.

Unfortunately the identities of the species scavenged by NO and C_2H_4 in the photolysis and thermolysis of silane have not been established. The chemistry of *none* of the hydrosilicon radicals nor that of silicon atoms is well understood.

The presence of low concentrations (4%) of ethylene, nitric oxide, or tetrafluoromethane does *not* inhibit the formation of the observed products (see Table IV). Neither the absolute nor the relative yields of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ are depressed. A 1:20:20 silane–ethylene–phosphine mixture yields, upon neutron irradiation, twice as much $^{31}SiH_4 + H_3{}^{31}SiSiH_3$ as are obtained products containing ethylene (see Figure 5). These results render unlikely the intervention of thermal $^{31}SiH_3$ radicals in the formation of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$. This interpretation is proposed although the efficiencies of these scavengers toward silyl radicals are not known, and product-forming steps including silyl radicals are quite plausible.

$$^{31}SiH_3 + SiH_4 \longrightarrow {}^{31}SiH_4 + SiH_3$$

$$^{31}SiH_3 + SiH_3 \longrightarrow H_3{}^{31}SiSiH_3$$

The expectation that CF_4 would scavenge silyl radicals is based on the remarkable abstraction of chlorine atoms from chlorobenzene by triphenylsilyl radicals[27]

$$(C_6H_5)_3Si + C_6H_5Cl \longrightarrow (C_6H_5)_3SiCl + C_6H_5\cdot$$

and on the large difference between C–F and Si–F bond strengths (19 kcal/mole).[28]

Strausz and coworkers report that the presence of 10% NO does *not* affect the yield of $CH_3SiH_2SiH_2CH_3$ from the far-ultraviolet photolysis of methylsilane.[29] The product is thought to arise from a reaction of a *divalent* silicon intermediate.

$$CH_3SiH_3 \xrightarrow{h\nu} CH_3SiH\colon + H_2$$

$$CH_3SiH\colon + CH_3SiH_3 \longrightarrow CH_3SiH_2SiH_2CH_3$$

Thus the scavenger experiments reported here seem compatible with the intermediacy of ^{31}Si, ^{31}SiH, and $^{31}SiH_2$ acting either alone or in concert.

Further information about the nature of the reactive intermediates has been obtained from the irradiation of phosphine–ethylene mixtures. A low concentration of ethylene does not inhibit the formation of $^{31}SiH_4$ and $H_3{}^{31}SiSiH_3$ from phosphine–silane mixtures, and no additional volatile products are observed. But when 1:1 phosphine–ethylene mixtures are irradiated with fast neutrons, six volatile radioactive products are obtained. Absolute yields are low, the total volatile radioactivity accounting for only 7 ± 3% of the ^{31}Si produced. The products consist of $^{31}SiH_4$, $^{31}SiH_3CH_2CH_3$, and four additional compounds whose chromatographic characteristics indicate that they include the elements of at least one ethylene molecule.

Ethylsilane formation in thermal experiments has been ascribed to the addition of silyl radicals to ethylene.[26]

$$SiH_4 \longrightarrow \cdot SiH_3 + H\cdot$$

$$\cdot H + SiH_4 \longrightarrow \cdot SiH_3 + H_2$$

$$\cdot SiH_3 + CH_2{=}CH_2 \longrightarrow SiH_3CH_2CH_2\cdot$$

$$SiH_3CH_2CH_2\cdot + SiH_4 \longrightarrow SiH_3CH_2CH_3 + \cdot SiH_3$$

Indeed an alternative mechanism involving silyl radicals

$$SiH_4 \longrightarrow \cdot SiH_3 + \cdot H$$

$$\cdot H + CH_2{=}CH_2 \longrightarrow CH_3CH_2\cdot$$

$$\cdot SiH_3 + CH_3CH_2\cdot \longrightarrow SiH_3CH_2CH_3$$

is excluded by the observation[30] that SiH_4 is a *much* better scavenger of hydrogen atoms than is ethylene. The intervention of other silicon species, ^{31}Si, ^{31}SiH, and $^{31}SiH_2$, in the formation of ethylsilane has not, however, been precluded.

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(25) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).

(26) D. G. White and E. G. Rochow, *ibid.*, **76**, 3897 (1954).

(27) J. Curtice, H. Gilman, and G. S. Hammond, *ibid.*, **79**, 4754 (1957). We thank Professor Hammond for calling our attention to this work.

(28) E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Co., New York, N. Y., 1963, p 54, Table 3.1.

(29) O. P. Strausz, K. Obe, and W. K. Duholke, *J. Am. Chem. Soc.*, **90**, 1359 (1968).

(30) H. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964).

The small yield of ethylsilane (8 ± 1% of the total volatile radioactivity) found in these experiments tends once again to cast doubt on the intervention of thermal silyl radicals.

The major product from the phosphine–ethylene system seems to be $^{31}\mathrm{SiH_3CH_2CH_2PH_2}$, a compound not previously reported. The identification is based on the following observations. (1) The chromatographic behavior is in accord with this formula. On a stationary phase (SF-96) which discriminates according to substrate boiling point, but *not* substrate polarity, the retention time of the major product is greater than that of diethylsilane but less than that of silacyclopentane. This brackets the boiling point of the unknown between 60 and 65°, a reasonable value for $\mathrm{SiH_3CH_2CH_2PH_2}$. On a stationary phase (dimethylsulfolane) which discriminates according to polarizability as well as boiling point, the retention time of the unknown is greater than that of silacyclopentane, the highest boiling $\mathrm{C_4SiH}_n$ compound known. This is compatible with the presence of a polar $\mathrm{PH_2}$ group in the unknown product. (2) None of the major product from the phosphine–ethylene system is produced when phosphine is replaced by trimethylphosphine as the silicon precursor (see Table VI). $^{31}\mathrm{SiH_4}$ and $^{31}\mathrm{SiH_3}$-$\mathrm{CH_2CH_3}$ are, however, obtained. (3) The yield of the major product appears to pass through a *maximum* as a function of the phosphine:ethylene ratio (see Table VI). Observtions 2 and 3 both indicate that the elements of the phosphine molecule are present in the major product. Three minor products from the phosphine–ethylene system remain unidentified.

Indication of a Common Intermediate in the Phosphine–Silane and Phosphine–Ethylene Systems. Silane and ethylene compete for a common intermediate. This is established by experiments in which small amounts of silane are added to 1:1 phosphine–ethylene mixtures prior to neutron bombardment (see Figure 5). A decrease in the yield of the product tentatively identified as $^{31}\mathrm{SiH_3CH_2CH_2PH_2}$ is accompanied by an increase in the yields of $^{31}\mathrm{SiH_4}$ and $\mathrm{H_3{}^{31}SiSiH_3}$ as the concentration of nonradioactive silane is increased. The ratio of $^{31}\mathrm{SiH_4}$ to $\mathrm{H_3{}^{31}SiSiH_3}$ varies in the manner previously found for small ratios of nonradioactive silane to phosphine. Thus ethylene reacts with the intermediate X which participates in product-determining steps in the silane–phosphine system. A formal description of the mechanism proposed for the phosphine–ethylene–silane system simply adds one step to the kinetic scheme already presented.

$$\mathrm{X + CH_2{=}CH_2 \xrightarrow{\sigma_5} {}^{31}SiH_3CH_2CH_2PH_2}$$

The observed efficiency of silane in diverting an intermediate from reaction with ethylene gives a ratio of reaction cross sections $(\sigma_1 + \sigma_2)/\sigma_5 = 11 \pm 3$. This does not imply that ethylene does not react with recoiling silicon species efficiently. Reactions which produce *volatile* products are, however, more efficient with silane than with ethylene. Since the absolute yields of $^{31}\mathrm{SiH_4}$ and $\mathrm{H_3{}^{31}SiSiH_3}$ are lower from phosphine–silane–ethylene mixtures than from phosphine–silane mixtures containing equal amounts of silane, it is clear that ethylene does react to form an involatile product with efficiency greater than that of phosphine.

Summary

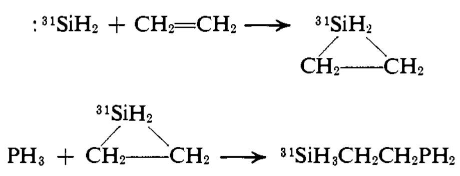
The reactions of recoiling silicon atoms produced by the transmutation of phosphorus in phosphine–silane mixtures have been found to produce with equal efficiency involatile products from interaction with phosphine and volatile products ($^{31}\mathrm{SiH_4}$ and $\mathrm{H_3{}^{31}SiSiH_3}$ in 1:5 ratio) from interaction with silane. Production of a volatile product, $^{31}\mathrm{SiH_4}$, from reactions with phosphine also takes place with low efficiency. Linear yield *vs.* reaction mixture composition curves for $^{31}\mathrm{SiH_4}$ and $\mathrm{H_3{}^{31}SiSiH_3}$ indicate that the reaction cross sections for product-determining steps are in constant ratio over the concentration range 0–80% $\mathrm{SiH_4}$. This implies either that silane is equally reactive toward hot and thermal recoiling silicon species or that the product-determining steps occur over an energy range small enough that relative reactivities do not change. A moderator experiment provides evidence that there is a "hot" reaction in the sequence which converts recoiling silicon atoms into the observed stable products.

It is tempting to ascribe this "hot" reaction to ^{31}Si atoms, but other possible reactive intermediates, ^{31}SiH and $^{31}\mathrm{SiH_2}$, might also undergo reactions in kinetically or electronically excited states. The yield curves can be accommodated by a competition between $\mathrm{PH_3}$ and $\mathrm{SiH_4}$ for a single intermediate or a set of intermediates formed in constant ratio. Thermal silyl radicals, $^{31}\mathrm{SiH_3}$, have been excluded from reactions leading to the observed products on the basis of scavenger experiments and the product spectrum of reactions of recoiling silicon atoms in phosphine–ethylene mixtures. The paucity of information about the thermal chemistry of simple silicon radicals makes it difficult to determine the roles of ^{31}Si, ^{31}SiH, $^{31}\mathrm{SiH_2}$, and $^{31}\mathrm{SiH_3}$ in the reported experiments.

A plausible but not unique set of product-forming steps which accounts for the observed products is

$$\mathrm{:{}^{31}SiH_2 + SiH_4 \longrightarrow H_3{}^{31}SiSiH_3}$$

$$\mathrm{:{}^{31}SiH_2 + SiH_4 \longrightarrow {}^{31}SiH_4 + :SiH_2}$$



$$\mathrm{:{}^{31}SiH_2 + CH_2{=}CH_2 \longrightarrow {}^{31}SiH_2(CH_2CH_2)}$$

$$\mathrm{PH_3 + {}^{31}SiH_2(CH_2CH_2) \longrightarrow {}^{31}SiH_3CH_2CH_2PH_2}$$

It is clear that equally plausible steps may be written involving ^{31}Si and ^{31}SiH either alone or in concert. The study of the reactions of recoiling silicon atoms is being continued.

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