Reactions with Silane of Silicon Atoms recoiling from $^{30}Si(n,\gamma)^{31}Si$

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THE chemistry of atomic silicon is under active investigation.[1,2] We report the product spectrum obtained from reactor-neutron irradiation of normal silane, and the effect of added ethylene, phosphine, and ammonia on product yields (see Table). In these experiments ^{31}Si atoms ($t_{\frac{1}{2}}$ 2·65 hr.) are produced by the nuclear transformation $^{30}Si(n,\gamma)^{31}Si$. Silane, disilane, and trisilane are the sole radioactive products sufficiently volatile to be identified by conventional radio v.p.c. techniques.[2]

Product yields from reactor-neutron irradiation of silane[a]

Substrate	Total volatile activity	Yields[b]		
		$^{31}SiH_4$	$^{31}SiSiH_6$	$^{31}SiSi_2H_8$
SiH_4	118±19	17± 3	40± 6	14±2
SiH_4–C_2H_4 (1 : 1)	44± 7	3± 1	9± 1	2±1
SiH_4–NH_3 (19 : 1)	219±35	27± 4	93±15	15±2
SiH_4	95±15	8± 1	27± 4	8±1
SiH_4–C_2H_4 (19 : 1)	98±16	6± 1	19± 3	14±2
SiH_4–PH_3 (1 : 1)	340±54	67±11	103±16	16±3

[a] All samples 2·2 ± 0·1 atm., irradiated 3 min. at 10^{12} neutrons/cm.^{2} sec.
[b] Thousands of counts above background extrapolated to common time.

The formation of trisilane is striking, since no trisilane has been detected in reactions of silane with ^{31}Si atoms produced from phosphine by the nuclear transformation $^{31}P(n,p)^{31}Si$. The radioactive products from phosphorus transmutation in the presence of silane consist of silane and disilane in the ratio 0·17 ± 0·04 : 1.[2]

Thus the chemistry of recoiling silicon atoms depends on their mode of formation. The following factors may be involved. (*a*) The kinetic energy of ^{31}Si atoms during reaction may depend on their mode of formation as does their initial recoil energy. The (n,γ) process produces ^{31}Si atoms with only *ca.* 10^2 ev recoil energy while the (n,p) process produces ^{31}Si with *ca.* 10^5 ev recoil energy. If product-determining reaction processes can occur at energies of 10^2 ev or above with cross sections which differ from those at lower energies, then different product spectra would be expected from the (n,γ) and (n,p) processes. (*b*) Due to the lower recoil energy, bond rupture may not be complete in the transmuted precursor molecule following (n,γ) activation.† Thus the reactive intermediates may differ in the two modes of formation of ^{31}Si. Free ^{31}Si atoms, formed by the (n,p) process, may be totally absent in the chemistry initiated by (n,γ) production of ^{31}Si. (*c*) Charge neutralization of ^{31}Si ions formed by the (n,γ) process may be incomplete, and ions may be important reaction intermediates in this process. Calculations based on the resonance rule[3] indicate that cross-sections for the neutralization of Si^+ reach maxima at energies of 10^4 ev,[2] well above the recoil energy of ^{31}Si from the (n,γ) transformation.

The effect of added ammonia and phosphine is to raise the yields of observed products (see Table). Since N–H and P–H bonds are stronger than Si–H, and since no new products are observed, it is unlikely that enhanced yields are due to hydrogen abstraction from the addenda or to formation of Si–N and Si–P bonds. The lower ionization potentials of ammonia (10·15 ev) and phosphine (10·0 ev) *versus* silane (12·2 ev) may however facilitate the neutralization of ionic intermediates. The observed products may result from the reactions of neutral species formed upon neutralization of ionic intermediates. The chemical differences between the (n,γ) and (n,p) modes of formation of recoiling silicon atoms seem thus to be related to the incursion of charged species in the chemistry which follows (n,γ) activation.

The presence of a large amount of ethylene causes a decrease in the yields of the observed products. No new products are observed. The effect of ethylene may be to trap intermediate

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† The internal energy available for bond rupture may be as small as 1/35 of the recoil energy for $^{31}SiH_4$.

radicals or ions. Since ethylene also has a lower ionization potential (10·56 ev) than silane, competing effects may be operative.

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