$\simeq$ 1.0 kcal/mole for the equilibrium equatorial $CH_3 \rightleftarrows$ axial CH_3. (2) In 7-ethyl-α,α-d_2-7,12-dihydropleiadene, the high-field methyl singlet is assigned to the *axial* C_7–CD_2CH_3 group, as in the 7-methoxy-7,12-dihydropleiadene conformers,[7] and the C_7-methine signals (seen clearly in the C_{12}-d_2 compounds) assigned as above, with the high-field signal arising from the equatorial proton. K_{eq} varies somewhat with temperature and is *ca.* 1.1 at $-20°$, giving $\Delta F°_{253} \simeq 0.0$ kcal/mole.[9] The noteworthy result is that the ethyl group has no substantial preference for either position, whereas the methyl group greatly preferred the equatorial position. (3) Only one conformer was detectable in 7-isopropyl-7,12-dihydropleiadene. Since the single C_7-methine doublet ($J \simeq 10$ cps) corresponds closely with the equatorial C_{12} proton, the C_7-isopropyl group is therefore overwhelmingly axial! Assuming $K_{eq} \geq 20$, $\Delta F°_{253} \leq -1.5$ kcal/mole.

The above preliminary results show that the conformational energies of methyl, ethyl, and isopropyl groups in dihydropleiadenes differ by at least 2.5 kcal/mole. At present, we wish mainly to note that conformational preferences of simple alkyl groups in various molecular arrays can be quite different from each other, in sharp contrast with the situation in simple cyclohexanes.[10]

Acknowledgment. We are grateful to the National Science Foundation for generous support of this research.

(9) More accurate measurements are needed to give meaningful values for $\Delta H°$ and $\Delta S°$ for 7-ethyl-DHP, although preliminary results suggest that *axial* 7-ethyl-DHP has the greater entropy.

(10) This has already been observed to an extent in 2-alkylcyclohexanones but the effect is smaller than in our examples; see also R. D. Stolow, *J. Am. Chem. Soc.*, **86**, 2170 (1964).

(11) Alfred P. Sloan Foundation Fellow, 1963–1967.

Peter T. Lansbury,[11] Andrew J. Lacher
Department of Chemistry, State University of New York at Buffalo
Buffalo, New York 14214

Received June 21, 1966

Reaction of Recoiling Silicon Atoms with Phosphine and Silane

Sir:

We wish to report our observations on the chemistry of recoiling silicon atoms in gaseous phosphine and phosphine–silane mixtures. These experiments represent a beginning toward the exploration of the hitherto unknown chemistry of atomic silicon.[1] 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 reaction of silicon atoms.

In these experiments free silicon atoms were produced from phosphine by nuclear techniques. Gaseous phosphine at *ca.* 2 atm pressure in quartz ampoules was irradiated with a flux of *ca.* 10^8 neutrons/cm^2 sec from the nuclear transformation $Be^9(d,n)B^{10}$ induced by a 20-μa current of 6-Mev deuterons accelerated by the Washington University Medical Cyclotron. The fast-neutron irradiation of P^{31} (natural abundance 100%) is known to yield Si^{31} (half-life 2.62 hr) from the nuclear transformation $P^{31}(n,p)Si^{31}$ with calculated cross-section 77 mbarns. The recoil energy of a Si^{31} atom formed under these conditions is *ca.* 6×10^5 ev, thus ensuring the breakage of all bonds present in the precursor molecule. Calculations based on the adiabatic principle[2] indicate that Si^{31} atoms should reach the energy region of chemical reactions as neutral species.

When pure phosphine was irradiated, the sole radioactive product which was eluted by helium from a variety of vapor-chromatographic columns at room temperature was silane (SiH_4). The silane contained *ca.* 60% of the total volatile radioactivity in the reaction vessel as determined by the analytical system consisting of two flow counters monitoring respectively the gas stream entering and the gas stream leaving the vapor chromatograph.[3] Reaction products were identified by comparison of retention times on at least two different chromatographic columns with those of authentic samples. It may be safely assumed that the only radioactivity detected in these experiments was the β-decay of Si^{31}.

Addition of cold silane to the reaction mixture prior to neutron irradiation resulted in an increase in the yield of radioactive silane and the appearance of a new radioactive product, disilane (Si_2H_6). The presence of even a few per cent of cold silane in the reaction mixture was accompanied by a tenfold increase in the total yield of volatile radioactivity. Increasing the amount of cold silane in the reaction mixture to 50% increased the total yield of volatile radioactivity only slightly and did not seem to have a further effect on the yield of radioactive silane. The yield of radioactive disilane did, however, increase with increasing pressure of cold silane in the reaction mixture. The fraction of the total volatile activity contained in the silane plus disilane also increased with increasing pressure of cold silane in the reaction mixture. The results of a series of experiments at fixed phosphine pressures and varying silane pressures are shown in Table I.

In an effort to determine whether thermal energy silyl radicals ($\cdot SiH_3$) were necessary precursors to radioactive silane produced in these reactions, a 1:1 mixture of phosphine and ethylene was irradiated with neutrons. Ethylene is known to be an efficient scavenger for thermal energy silyl radicals.[4] The yield of radioactive silane was only slightly (<40%) reduced in this experiment. In addition to radioactive silane, other volatile radioactive products were detected which resulted from attack on ethylene by silicon-containing species. These products will be described in a future report.

When a small amount (2%) of ethylene was added to a mixture of silane and phosphine (SiH_4:PH_3 = 0.82) prior to neutron irradiation, in order to scavenge ther-

(1) For recent reports in which the possible occurrence of silicon atoms is considered, see (a) M. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964); (b) D. Snediker and W. W. Miller, "Recoil and Radiation Chemistry of Silanes," in "A Report of Current Research Activities of the Department of Chemistry," The Pennsylvania State University, July 1965; (c) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).

(2) (a) H. S. W. Massey, and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p 441; (b) M. A. El-Sayed, P. J. Estrup, and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

(3) The analytical method is essentially a two-counter version of that described by R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

(4) D. G. White and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 3897 (1954).

Table I.[a] Yields of Si^{31}-Labeled Products from Reactions of Si^{31} with PH_3–SiH_4 Mixtures[d]

SiH_4:PH_3 ratio	Total volatile activity[b,e]	$Si^{31}H_4$[b]	$Si^{31}SiH_6$[b]	$\frac{Si^{31}SiH_6}{Si^{31}H_4}$	$\frac{Si^{31}H_4 + Si^{31}SiH_6{}^{c}}{\text{total volatile activity}}$
0	1047 ± 61.7	639 ± 58	0	0	0.64 ± 0.07
0.29	9127 ± 113	1434 ± 50	5281 ± 95	3.7 ± 0.11	0.73 ± 0.02
0.76	9586 ± 109	1332 ± 52	6702 ± 99	5.1 ± 0.15	0.84 ± 0.02
0.85	10995 ± 114	1534 ± 68	8305 ± 128	5.4 ± 0.15	0.89 ± 0.02

[a] All samples contained 2.2 ± 0.3 atm of PH_3 and were simultaneously irradiated 1 hr with an equal (±5%) flux of fast neutrons. [b] Yields are given as counts above background extrapolated to a common time to correct for decay. [c] These ratios are minimum values. Calibrations indicate that the total activity counter is slightly more efficient than the counter monitoring separated products. [d] Uncertainties are standard deviations calculated from total numbers of counts recorded in single experiments. [e] The total volatile activities are approximately 5% (for SiH_4:PH_3 = 0) and 50% (other ratios) of the total activities produced in the reaction vessels.

mal silyl radicals, the ratio of radioactive disilane to radioactive silane among the products increased slightly (to 7.5), but the fraction of the total volatile radioactivity contained in the silane and the disilane decreased to 55%. Again products resulting from attack by silicon-containing species on ethylene were detected.

These results indicate that the radioactive products silane and disilane do not result from the reactions of silyl radicals at thermal energies.[5] Rather it seems that radioactive silane arises from the reactions of species not efficiently scavenged by ethylene. The silane precursors may be translationally or vibrationally excited and not discriminate between ethylene and phosphine, thus accounting for the low degree of intervention by ethylene in the formation of radioactive silane. On the other hand, scavenging may be inefficient because the silane precursors are relatively unreactive toward ethylene.

The formation of radioactive disilane even at low concentrations of cold silane suggests that a thermal energy species could be a precursor of disilane. The disilane precursor discriminates markedly between silane and phosphine but is not efficiently scavenged by ethylene. More data on the competition between silane and phosphine for the disilane precursor will facilitate the determination of the hot and thermal contributions to the formation of disilane. A reasonable suggestion for the disilane precursor is the silicon analog of methylene, silylene[6] (:SiH_2).

$$:\mathrm{Si^{31}H_2} + \mathrm{SiH_4} \longrightarrow \mathrm{H_3Si^{31}SiH_3}$$

Certainly other simple species could react with silane to give products which, lacking intramolecular paths to

$$:\dot{\mathrm{Si}}\mathrm{^{31}H} + \mathrm{SiH_4} \longrightarrow \mathrm{H_2Si^{31}}\dot{\mathrm{Si}}\mathrm{H_3}$$

$$:\underset{\cdot}{\dot{\mathrm{Si}}}{}^{31} + \mathrm{SiH_4} \longrightarrow \mathrm{H}\ddot{\mathrm{Si}}\mathrm{^{31}SiH_3}$$

stable products, could react further to yield disilane.[7] Efforts to elucidate the mechanisms of these reactions are being continued and extended to other reaction substrates.

Acknowledgment. The authors wish to thank Professor Richard Wolfgang for his kind advice and abundant encouragement. The assistance of Dr. Michel M. Ter-Pogossian, Mr. S. Alan Bock, and Mr. John Hood is gratefully acknowledged. This work was begun with support from NASA under the Washington University multidisciplinary research grant and is being continued under a basic research grant from the National Science Foundation.

Peter P. Gaspar, Brian D. Pate, William Eckelman
Department of Chemistry, Washington University
St. Louis 5, Missouri

Received June 6, 1966

---

[5] Note that disilane does arise from dimerization of silyl radicals in the photolysis[1a,c] and pyrolysis[4] of silane.

[6] The previously used term "silene" (*e.g.*, P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964)) should be reserved for compounds of π-bonded silicon. The generic term for a divalent silicon species analogous to "carbene" is clearly "silicene."

[7] A referee has pointed out that the present data can be explained by assuming the production of *two* reactive species, such as two electronic states of the silicon atom, in constant ratio. Of these one reacts much more efficiently with phosphine than with silane and gives radioactive silane. The other species could react with comparable efficiencies with phosphine to give an involatile product and with silane to give disilane. Thus the increase in disilane yield with cold silane concentration is explained.

Mechanism of Metal-Catalyzed Hydrogenation and Exchange. The Phenyl Effect

Sir:

We wish to report the discovery of an unusual substituent effect in the metal-catalyzed hydrogenation of C–C double bonds. Recognition of the effect allows correlation of a mass of seemingly contradictory and unrelated data and opens new paths for gaining deeper understanding of the nature of surface species.

The effect is quite simple: a phenyl substituent at the C–C double bond increases the extent of pure 1,2-*cis* addition relative to other processes such as exchange, racemization, double bond migration, and *cis–trans* isomerization. In certain instances the phenyl effect is so pronounced as to yield 98% 1,2-*cis* addition over palladium, a catalytic surface on which these other processes usually occur with ease. We have observed the effect on a number of compounds, and similar evidence exists in the literature.

Our evidence stems from nmr and mass spectral studies of deuterium distributions acquired by substituted ethylenes and their reduction products during liquid phase deuteriogenation over 5% palladium on charcoal and 5% platinum on charcoal. Experiments and analyses were conducted as previously described[1,2] and pertinent data are presented in Table I for palladium. In every instance substitution of phenyl for hydrogen, methyl, or carbomethoxyl increases 1,2-*cis* addition relative to exchange, *i.e.*, deuterium distributions are more symmetrical and dideuterio species are more prevalent. However, Table I reveals only part

---

[1] For experimental and nmr procedures see G. V. Smith and J. A. Roth, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam,* 379 (1964).

[2] For mass spectral procedures see G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962).