TABLE IV

SUMMARY OF CONSTANTS

Reaction μ = 2.00	10°	25°	40°	
$UO_2^{++} + Cl^- = UO_2Cl^+$	0.58	0.88	1.14	
$UO_2^+ + NO_3^- = UO_2NO_3^+$	0.30	0.24	0.17	
$UO_2^{++} + SO_4 = UO_2SO_4$	63	76	96	
$UO_2^{++} + 2SO_4 = UO_2(SO_4)_2^=$	5.8×10^2	7.1×10^2	8.2×10^2	
$UO_2\ ^+ + HSO_4^- = UO_2SO_4 + H^+$	6.1	6.4	6.5	
$UO_2^{++} + HF = UO_2F^+ + H^+$	55	26	21	
25°, μ =	0.05	0.25	0.50	1.00
$UO_2^{++} + HF = UO_2F\ + H$	51	37	24	27

TABLE V

FREE ENERGY, HEAT CONTENT AND ENTROPY CHANGES AT 25°, IONIC STRENGTH 2.00, FOR THE REACTIONS: $UO_2^{++} + nX^- = UO_2X_n^{+2-n}$

Complex formed	ΔF, kcal./mole	ΔH, kcal./mole	ΔS, kcal./deg./mole
UO_2Cl^+	0.08	3.8	12
UO_2SO_4	−2.6	2.3	16
$UO_2(SO_4)_2^=$	−3.8	1.4	18
UO_2F^+	−1.9	−5.4	−12

The constants for sulfate complexing are in general agreement with values measured by other methods.[1d,3] The distribution ratios listed in Table I have been corrected for change in hydrogen ion concentration by formation of bisulfate ion. A value of 0.084 for the ionization constant of bisulfate at 25° and ionic strength 2.00 was used in these calculations.[7] At 10° and 40° the values of the ionization constant used were 0.097 and 0.068, respectively. These were estimated from data for the variation of the constant with temperature at low ionic strength.[12] The extraction data indicate the formation of at least two sulfate complexes, in agreement with the results of Ahrland.[1d] Betts and Michels[3] did not report a second complex in their studies.

The extent of complexing of uranyl by fluoride found here is of the same magnitude as that estimated from ion-exchange data.[4] There was no indication of the formation of a second fluoride complex at the concentrations of fluoride employed. The distribution ratios in Table I have been corrected for change in hydrogen ion concentration by formation of hydrogen fluoride. It was assumed that ionization of hydrogen fluoride was negligible, the ionization constant being 6.71×10^{-4} at 25°.[13] An approximate value for the activity constant was obtained assuming the Debye–Hückel equation holds up to an ionic strength of 2.00. A plot of log k_{01} *versus* $\mu^{1/2}/(1 + 1.972\ \mu^{1/2})$ gave a value of about 60 on extrapolation to zero ionic strength. Kraus and Nelson[2] used this equation for estimation of the activity constant for formation of the uranyl chloride complex.

The distribution ratios obtained with salt solutions of different concentrations are given in Table III. In perchlorate media the ratio first increases somewhat, and then gradually decreases as the salt concentration is increased. In chloride media the ratio increases steadily as the salt concentration is increased, the increase being somewhat more rapid at about 4.5 *M* chloride. In nitrate media the ratio rises to 1.44 at 1.00 *M* nitrate and then remains essentially constant up to 7.00 *M* nitrate. The distribution ratios in all three media approach the same value as the concentration is decreased to 0.05 *M*.

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[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 430.

[13] H. H. Broene and T. De Vries, THIS JOURNAL, **69**, 1644 (1947).

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY]

Reactions of Silane with Unsaturated Hydrocarbons

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The reactions of silane with ethylene, acetylene and vinylsilane have been investigated in a system which circulated the gaseous reactants continuously through the reaction zone. Ethylene and silane at 450–510° produced ethylsilane, diethylsilane and smaller quantities of disilane, trisilane and a compound believed to be ethyldisilane. Acetylene and silane at 460–510° gave a small amount of vinylsilane, but the bulk of the product consisted of ethynylsilane, particularly ethynyldivinylsilane. With photochemical activation, the principal products were ethylsilane, *n*-butylsilane and 1,4-disilylbutane from silane and ethylene, and vinylsilane from silane and acetylene. Irradiation of a mixture of silane and vinylsilane under similar conditions gave 1,2-disilylethane, but at the same time a large amount of the vinylsilane polymerized to form a white solid. This solid was also produced, along with a volatile dimer, when vinylsilane alone was irradiated. Free-radical mechanisms are suggested for these reactions and are supported by the relative proportions of products.

Introduction

Recent studies have shown the alkylsilanes are formed when silane is heated with an olefin. The addition proceeds at moderate temperature when the reactants are under pressure; for example, Hurd[2] obtained ethyl-, diethyl- and triethylsilane by heating silane and ethylene to 100° under pressure. The reaction with ethylene at atmospheric pressure has been described by Fritz,[3] who allowed a mixture of silane and ethylene to react at 450° in a static system for 80 minutes. Ethyl-, diethyl-

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[1] Abstracted from a thesis presented by David G. White to the Faculty of Arts and Sciences of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] D. T. Hurd, U. S. Patent 2,537,763 (1951).

[3] G. Fritz, *Z. Naturforsch.*, **7b**, 207 (1952).

and triethylsilane were formed, but the product also included a number of methylsilanes and compounds of much higher molecular weight. The exact course of the addition could not be determined, since further reaction of the initial products was extensive under these conditions. However, Fritz found that the reaction began at about 380°, and since silane is decomposed at about this temperature,[4] he concluded that the initial step in the complex free-radical mechanism involved must be the formation of hydrogen atoms and silyl (SiH_3) radicals from silane.

We have completed a study of the thermal reaction of silane and ethylene at normal pressures in a flow system which permitted isolation of the initial products. The behavior of silane when heated with acetylene or alkanes under these conditions also has been examined.

Although silane at pressures up to 75 mm. does not absorb ultraviolet radiation of wave length greater than 1850 Å., it is decomposed by radiation from a mercury arc when the gas contains mercury vapor.[5] We have found that the mercury-photosensitized decomposition of silane in the presence of ethylene, acetylene or vinylsilane leads to the formation of alkylsilanes. Furthermore, vinylsilane alone polymerizes when activated in this manner.

Experimental

Apparatus.—The gaseous mixture of silane and hydrocarbon was circulated by a motor-driven bellows through a quartz tube 19 mm. in diameter which could be heated or irradiated. Two Pyrex check valves, located near the bellows, allowed the gases to flow in only one direction around the closed circuit. In series with the bellows and tube was a trap which could be cooled. Gases could be introduced or removed from the reaction system through a conventional high vacuum apparatus.

The temperature of the heated tube was determined with an iron–constantan thermocouple, the junction of which was placed against the outer wall of the tube at the center of the furnace. Since the thermocouple was not positioned within the tube, the temperature values given must be somewhat higher than the true temperatures.

In those experiments where silane–hydrocarbon mixtures were activated by ultraviolet light, the furnace was replaced by a mercury-vapor discharge lamp (Hanovia Chem. and Mfg. Co.). The lamp, made from 7-mm. quartz tubing, was in the form of a helix with an outer diameter of 50 mm. and a length of 5 in. A 5000-volt transformer operated the discharge and the current in the secondary was measured at 110 ± 10 ma. No attempt was made to reflect the radiation emitted outward from the reaction tube.

The bellows was driven at the rate of 1·1 to 1·3 cycles per second in all of the experiments. Approximate values of the gas velocity through the reaction tube, calculated from its dimensions and the displacement of the bellows, varied from 110 to 130 cm. per second for those experiments at room temperature and from 280 to 380 cm. per second for those at 450–600°.

Materials.—Silane was prepared by the reduction of silicon tetrachloride (Stauffer Chemical Co., tech.) with a suspension of lithium aluminum hydride in diethyl ether and purified by a distillation from a bulb at the m.p. of isopentane (−160°).[6] Ethylene of 99.5% purity was taken directly from a Matheson Co. cylinder; the acetylene (Linde Air Products Co.) was distilled from a bulb at −130° before use. The vacuum technique of Finholt[6] was used to prepare vinylsilane from vinyltrichlorosilane (Anderson Laboratories, Inc.) and lithium aluminum hydride suspended in dioxane. Purification of this compound was achieved by two distillations at −116° followed by condensation at −131°. Its b.p. extrapolated from vapor pressure measurements was −23° at 760 mm.; the reported value is −22.8°.[7]

Procedure.—A silane–hydrocarbon mixture of known composition was prepared by measuring the pressure of each reactant in a calibrated volume of the vacuum apparatus. The total amount of mixture was adjusted so that the initial pressure in the reaction system would be slightly under one atmosphere. (The total volume of the reaction system when the bellows was at the midpoint of its stroke was 850 ml.) After evacuation of the system, the mixture was introduced from the vacuum apparatus and condensed into the trap with liquid nitrogen. Vaporization and circulation of the gases through the heated or irradiated tube was then begun.

During the course of some experiments, the pressure fell considerably because of the condensation of a large amount of product in the trap. Since the operation of the bellows required an internal pressure of about 500 mm. or greater, it was necessary in these cases to introduce nitrogen at atmospheric pressure into the system from the vacuum apparatus.

At the completion of an experiment, the furnace or mercury discharge was turned off, and a bath of liquid nitrogen was placed about the trap while the gases were circulated for another 10 to 15 minutes. More nitrogen was introduced at this point to maintain the pressure in the system. The gases not condensed at this temperature (including any hydrogen or methane produced in the reaction) were then removed by the pumps, and the product in the trap was distilled into the vacuum apparatus for separation and analysis.

Analysis of Product.—Separation of the products was achieved by a series of fractional distillations and condensations; the procedure employed has been described by Sanderson.[8] The yield of each fraction was measured by observing the pressure exerted when the entire fraction was vaporized into a calibrated column. Vapor pressures at temperatures below room temperature were measured in the conventional manner, and those above room temperature were determined by means of a modified isoteniscope, in which a fixed amount of mercury served as the confining liquid. The molecular weight of a sample was calculated from its vapor density.

Compounds containing silicon–hydrogen or silicon–silicon bonds hydrolyze in bases to give one mole of hydrogen per mole of compound for each silicon–hydrogen or silicon–silicon bond present in the molecule.[9] In our experiments these quantitative hydrolyses were performed by condensing about 10–20 mg. of the sample into a tared bulb of 125-ml. capacity. About 5 ml. of a 2 *M* solution of potassium hydroxide in ethanol was introduced through the stopcock of the bulb, and the bulb was allowed to stand with occasional shaking for 3 to 4 hours. The evolved hydrogen was pumped by a mercury piston through a trap immersed in liquid nitrogen and into a gas buret.

All analyses for carbon, hydrogen and silicon were conducted by the Microchemical Laboratory of the Massachusetts Institute of Technology.

Infrared spectra of the gaseous products between 2 and 16 μ were obtained with a Baird recording spectrophotometer. Frequently the spectrum served as the only identifying property of a small amount of product, and unless other information is given it should be assumed that the products were identified in this way. In order that positive identifications could be made on this basis, many silanes were prepared by reduction of the corresponding chlorosilanes with lithium aluminum hydride[6] and their spectra (and that of tetramethylsilane) were recorded at various pressures. Methylsilane, dimethylsilane, trimethylsilane, ethylsilane, diethylsilane, silane, disilane, vinylsilane and 1,2-disilylethane were prepared and studied in this manner. Each spectrum showed distinctive absorption bands even at a gas pressure of 5 mm. in a cell of 40 mm. path length.

1,2-Disilylethane, not previously reported, was prepared

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[4] G. Fritz, *Z. Naturforsch.*, **7b**, 507 (1952).

[5] H. J. Emeleus and K. Stewart, *Trans. Faraday Soc.*, **32**, 1577 (1936).

[6] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

[7] S. Tannenbaum, S. Kaye and G. F. Lewenz, *ibid.*, **75**, 3753 (1953).

[8] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 91.

[9] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 164.

TABLE I

VAPOR PRESSURE OF 1,2-DISILYLETHANE

Temp., °C.	−63.5	−45.2	−22.6	0	29.1	33.0	35.6	37.6
P, mm. (obsd.)	2.0	9.2	38.0	124.0	417.2	481.2	526.0	564.5
P, mm. (from eq.)	2.04	8.2	35.7	116	410	482	541	566

from 1,2-bis-(trichlorosilyl)-ethane by the technique described by Finholt, *et al.*[6] Three grams (10 mmoles) of 1,2-bis-(trichlorosilyl)-ethane was introduced slowly into a suspension of 1.0 g. of lithium aluminum hydride in 10 ml. of di-*n*-butyl ether at 0°, and the product was separated by collecting the material which distilled at 0°. Ether was removed by two further distillations at −70°, and the bulk of the 1,2-disilylethane was condensed in a trap at −80°. The yield was 6.3 millimoles (63%). The vapor pressures of 1,2-disilylethane are given in Table I, wherein the first four values were measured at the melting points of chloroform, chlorobenzene, carbon tetrachloride and water, respectively. Data at and above room temperature were obtained with an isoteniscope using mercury as the confining liquid.

Calculation of the vapor pressure equation by the method of least squares gave

$$\log_{10} P_{\text{mm}} = 7.793 - 1563/T$$

At 760 mm. the extrapolated b.p. was 45°. By Stock's procedure[10] the m.p. was −102°.

Behavior of Silane and Alkanes.—Silane did not react with methane, ethane, propane or isobutane at temperatures between 440 and 610°. At 440–500°, some di-, tri- and tetrasilane were formed from the decomposing silane, and the yields of these products, particularly those of tri- and tetrasilane, were higher when the trap in the system was cooled to −78° with a Dry Ice–acetone-bath.

Only di-, tri- and tetrasilane were produced when a mixture of silane, ethane and hydrogen, containing mercury vapor, was irradiated at room temperature with a mercury discharge. A yellow-brown mirror of silicon (or of polymeric silicon hydride) was deposited in the quartz reaction tube.

Thermal Reaction of Silane and Ethylene.—A mixture of silane and ethylene was circulated for three hours through the heated tube with the results given in Table II. In these experiments no attempt was made to separate products with small differences in volatility; thus, the unreacted silane and ethylene distilled together at −145°, and when both disilane and ethylsilane were formed, the two compounds distilled at about −110°. The yields given in Table II refer to these fractions, and the approximate temperature at which each distilled has been indicated. The symbol A represents a compound which was tentatively identified as ethyldisilane, and the products which distilled at −40° (and the small amount of residue, the yield of which is not shown) were not identified. In each experiment, a thin layer of silicon was deposited on the wall of the reaction tube.

TABLE II

REACTION OF SILANE AND ETHYLENE AT 456–511°

C_2H_4, mmoles		22.2[a]	22.2	22.3	15.0	14.7
SiH_4, mmoles		7.44	7.26	7.35	14.7	14.6
t, °C.		494–511	498–511	456–478	497–510	456–464
Dist. *t*, °C.	Compounds	Fraction yield, mmoles				
−145	C_2H_4, SiH_4	15.0	17.9	26.9	10.45	26.8
−110	$EtSiH_3$, Si_2H_6	1.48[b]	1.44	0.31	1.72	0.46
− 70	Et_2SiH_2, Si_3H_8, A	1.71[c]	1.03[d]	0.19[d]	2.23	0.14
− 40	....	0.255	0.595	0.25	0.975	0.31

[a] Trap at room temperature. [b] $EtSiH_3$ only. [c] Et_2SiH_2 only. [d] No Si_3H_8.

Ethylsilane from the first experiment of Table II was purified by collecting only that material which condensed at −135°, and two distillations at −109° served to remove higher-boiling impurities. The sample had a molecular weight of 59.4 (calcd. for C_2H_8Si, 60.1), and hydrolysis of 0.707 millimole gave 2.05 millimoles of hydrogen, or 2.90 moles of hydrogen per mole. Its infrared spectrum was identical with that of ethylsilane prepared from ethyltrichlorosilane. Diethylsilane was purified by a distillation at −78° and condensation at −102°. A 0.705-millimole sample had a molecular weight of 90.5 (calcd. for $C_4H_{12}Si$, 88.4) and evolved 1.54 millimoles of hydrogen (2.18 moles of hydrogen per mole). Its infrared spectrum was the same as that of diethylsilane from diethyldichlorosilane.

In the remaining experiments shown in Table II, the trap in the system was cooled to −78°, and, as a result, a sharp band at 11.85 μ, characteristic of disilane, appeared in the spectra of the ethylsilane fractions. Similarly, the spectra of the diethylsilane fractions had bands at 10.62, 11.2–11.4 and 12.63 μ which were assigned to compound A. Some trisilane also was detected in the last two experiments. The relative concentrations of disilane and compound A in their respective fractions were estimated by observing the intensities of their infrared absorption bands relative to those of ethyl- and diethylsilane, respectively. The ratio of disilane to ethylsilane increased when the temperature of the heated tube was lowered, and also when the concentration of silane in the reactants was raised. The ratio of compound A to diethylsilane varied in the same manner. Similarly, the formation of trisilane was favored by a decrease in reaction temperature. If compound A contained a silicon–silicon bond and thereby possessed a relatively low thermal stability, then its formation would be expected to parallel that of disilane and trisilane. Also, since its volatility was close to that of diethylsilane, it is likely that its molecular weight is about the same. For these reasons, compound A was probably ethyldisilane, $C_2H_5Si_2H_5$.

Thermal Reaction of Silane and Acetylene.—Mixtures of silane and acetylene were circulated through the heated tube and a trap at −78° for three hours. Table III lists the results of three experiments; those compounds which constituted a small part of any one fraction are enclosed in parentheses.

The bulk of the unreacted acetylene distilled from the product at −140° but, in each case, the infrared spectrum of this fraction indicated that vinylsilane also was present. Beer's Law was used to calculate the percentage of vinylsilane in these mixtures, and the results are given in Table III. The fractions which distilled at −117° contained vinylsilane, together with lesser amounts of disilane and a third compound. Absorption bands at 3.02, 4.9 and 14.6 μ were attributed to this unidentified compound, and although the first two wave lengths are representative of the ethynyl group,[11] further conclusions as to its structure are not warranted. At least two compounds were present in the fractions which distilled at −70°; absorption typical of silicon–hydrogen bonds, vinyl groups and ethynyl groups was apparent in their spectra.

TABLE III

REACTION OF SILANE AND ACETYLENE AT 460–514°

C_2H_2, mmoles		22.2	15.0	14.6
SiH_4, mmoles		7.4	14.8	14.6
t, °C.		502–514	504–512	460–473
Dist. *t*, °C.	Compounds	Fraction yield, mmoles		
−160	$SiH_4(C_2H_2)$	4.26	6.55	12.3
−140	C_2H_2	12.85[a]	1.42	9.95
	$C_2H_4SiH_3$	0.085	0.035	0.065
−117	$C_2H_3SiH_3(Si_2H_6)$(?)	0.15	0.48	0.27
− 70	....	0.36	0.51	0.22
− 40	$(C_2H_3)_2C_2HSiH$	2.31	2.11	0.63

[a] No Si_2H_6.

Ethynyldivinylsilane distilled at −40° and was purified by a second distillation at this temperature. The original material was yellow, but the color faded somewhat on fractionation. The vapor pressures at 0 and 31.6° were 13.3 and 62.0 mm., respectively, and the molecular weight was

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(10) A. Stock, *Ber.*, **50**, 156 (1917).

(11) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

106 (calcd. for C_6H_8Si, 108.2). Two hydrolyses were performed: 0.0168 g. evolved 0.187 millimole of hydrogen and 0.0139 g. gave 0.160 millimole, corresponding to 1.18 and 1.22 moles of hydrogen per mole of compound, based on the experimental molecular weight. Since ethynyl groups attached to silicon are reported to hydrolyze readily to give acetylene,[12] 0.0817 g. of ethynyldivinylsilane was treated with alcoholic KOH in a bulb and allowed to stand overnight. Distillation at −135° gave 0.636 millimole of acetylene, or 0.825 mole of acetylene per mole of compound. An infrared spectrum of the ethynyldivinylsilane showed the presence of ethynyl and vinyl groups, and there was no absorption at 6.8–7.0 μ, a characteristic absorption band of the ethylsilanes.

Anal. Calcd. for C_6H_8Si: C, 66.61; H, 7.45. Found: C, 66.20; H, 7.47.

Small amounts of higher-boiling products remained after the distillations at −40°. During each experiment, a small quantity of a yellow solid appeared in the cold part of the reaction tube, and a thin layer of silicon was deposited in the heated area.

Photosensitized Reaction of Silane and Ethylene.—When silane–ethylene mixtures were introduced into a quartz vessel and irradiated at room temperature with a mercury-vapor discharge, a pronounced drop in pressure was observed. Only a small quantity of volatile product was formed, and the principal products were a yellow solid and a colorless oil, both of which evolved hydrogen on hydrolysis with base.

A much higher yield of volatile compounds was obtained when mixtures of silane and ethylene were circulated through the quartz tube and irradiated. The results of two experiments are given in Table IV; in each case, the trap in the system was cooled to −78° and the gases were irradiated for three hours, but in the second experiment, a pool of mercury was placed in the apparatus just ahead of the quartz tube in order to introduce an appreciable quantity of mercury vapor into the reactants. Unreacted silane and ethylene (and a trace of acetylene) were removed from the products by a distillation at −150°. The ethylsilane was identified by comparing its spectrum with that of pure ethylsilane. An additional band at 11.85 μ in the former indicated that a small quantity of disilane was present.

TABLE IV

PHOTOSENSITIZED REACTION OF SILANE AND ETHYLENE

		Expt. I	Expt. II[a]
C_2H_4, mmoles		17.8	17.95
SiH_4, mmoles		17.8	18.0
Dist. *t*, °C.	Compounds	Fraction yield	mmoles
−149	SiH_4, $C_2H_4(C_2H_2)$	33.9	29.5
−100	$EtSiH_3(Si_2H_6)$	0.14	0.47
− 56	*n*-$C_4H_9SiH_3$	0.15	0.71
− 22	$H_3SiC_4H_8SiH_3$	0.09	0.47

[a] Mercury vapor introduced.

The product which distilled at −56° was combined and redistilled at −63°. That portion which condensed at −78° was collected, and the vapor pressure was found to be 10 mm. at −33° and 66 mm. at 0°. These values are somewhat lower than the vapor pressure of *n*-butylsilane at these temperatures[6] (11 and 78 mm.). However, the sample was not tensiometrically homogeneous, and the following results suggest that the material did contain a small amount of a higher-boiling compound. Two determinations of the vapor density gave 89.9 and 90.3 for the molecular weight (calcd. for $C_4H_{12}Si$, 88.2), and when two samples were hydrolyzed, 3.08 and 3.24 moles of hydrogen were evolved per mole of compound (the higher value was obtained from a less volatile portion of the product). The only compounds that conform to the above data are the isomeric butylsilanes. Moreover, the infrared spectrum in the 10–14 μ region of a solution of this product in carbon disulfide was identical with that of *n*-butylsilane in the same solvent[13] except that one absorption band, attributed to the unknown impurity, was missing in the latter.

The remaining product was purified by distillation at −22° and condensation at −60°. Its vapor pressure was 8 mm. at 0° and 22 mm. at 20°; two determinations of the molecular weight gave 126.2 and 116.6 (calcd. for $C_4H_{14}Si_2$, 118.3). The hydrolysis of two samples yielded 5.50 and 6.10 moles of hydrogen per mole. Only two carbon–hydrogen vibrations (3.45 and 3.55 μ) were visible in its spectrum, but a third peak at a slightly lower wave length would be expected if methyl groups were present.[11] Therefore, the 1,4-disilylbutane structure was assigned to this substance.

Photosensitized Reaction of Silane and Acetylene.—Mixtures of silane and acetylene were passed over mercury and circulated through the quartz tube and the trap at −78° for three hours. The conditions of two experiments and the yields of products are given in Table V. In both experiments a yellow-brown mirror was deposited on the walls of the tube; presumably this solid reduced the transparency of the quartz and retarded the reaction, since the total yield of products was not increased appreciably when the time of irradiation was doubled.

TABLE V

PHOTOSENSITIZED REACTION OF SILANE AND ACETYLENE

		Expt. I	Expt. II
C_2H_2, mmoles		27.2	18.1
SiH_4, mmoles		8.94	17.9
Dist. *t*, °C.	Compounds	Fraction yield, mmoles	
−160	$SiH_4(C_2H_2)$	8.65	17.6
−140	C_2H_2	26.6	17.0
	$C_2H_3SiH_3$	0.17	0.25
−105	$C_2H_3SiH_3$	0	0.11
Residue	....	0.11	0.12

The fractions which distilled at −140° contained unreacted acetylene and an azeotrope with vinylsilane, and additional vinylsilane distilled at −105°. The percentages of vinylsilane in these fractions were derived from the spectra of the fractions and that of pure vinylsilane by applying Beer's Law; the amount of vinylsilane present in each is tabulated. The spectrum of the vinylsilane which distilled at −105° was identified with that prepared from vinyltrichlorosilane. A sample of this product had a molecular weight of 55 (calcd. for C_2H_6Si, 58.1) and evolved 3.3 moles of hydrogen per mole on hydrolysis.

Photosensitized Reaction of Silane and Vinylsilane.—A mixture of silane (18.0 millimoles) and vinylsilane (14.87 millimoles) was passed over mercury and irradiated for two hours. In this experiment the trap in the system was not cooled. A white solid was formed on the walls of the quartz tube, and the mercury lamp was moved several times during the two hours in order to expose clean surfaces of the tube. A considerable amount of non-volatile oil also was formed, but this was deposited throughout the apparatus and not confined to the quartz tube.

The volatile product was distilled and gave 15.33 millimoles of unreacted silane at −146°, 6.83 millimoles of unreacted vinylsilane at −114°, 0.43 millimole of 1,2-disilylethane at −65°, 0.08 millimole of a compound believed to be either (2-silylethyl)-vinylsilane or 1-ethyl-2-vinylsilane (see experimental section on photosensitized polymerization of vinylsilane) and 0.22 millimole of residue.

The 1,2-disilylethane fraction after purification had a vapor pressure of 2.7 mm. at −63.5° and 10.0 mm. at 45.2°; the values reported in Table I at these temperatures are 2.0 and 9.2 mm., respectively. The molecular weight of the fraction was 86.0 (calcd. for $C_2H_{10}Si_2$, 90.2), and hydrolysis of two samples gave 6.21 and 5.76 moles of hydrogen per mole. The spectrum of this fraction agreed closely with that of the 1,2-disilylethane prepared earlier, except that a small band at 12.5–12.7 μ in the former was absent in the latter. (The compound responsible for this band was also formed in small quantity when vinylsilane alone was irradiated.)

The product obtained in greatest yield was the white solid previously mentioned. This was washed with chloroform and dried at room temperature in a vacuum. The resulting product was insoluble in diethyl ether, benzene or carbon disulfide, and discolored but did not melt when

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(12) V. N. Volnov and A. Reutt, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1600 (1940).

(13) S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1953).

heated in a melting-point capillary. Hydrogen was evolved very slowly when it was treated with a 2 *M* solution of potassium hydroxide in ethanol, and hydrolysis of 0.01 g. was complete only after heating at 40° for several hours. Two hydrolyses in this manner gave 1.88 and 2.01 moles of hydrogen per gram atom of silicon, indicating a polymer of vinylsilane.

Anal. Calcd. for $(C_2H_6Si)_x$: C, 41.32; H, 10.41; Si, 48.27. Found: C, 38.80; H, 9.83; Si, 52.23, 51.20; sum, 100.34.

Photosensitized Polymerization of Vinylsilane.—When vinylsilane containing mercury vapor was irradiated, a pronounced drop in pressure was observed. The chief products were a non-volatile oil and a small quantity of white solid. Very little oil and much more solid were formed when vinylsilane was irradiated in the flow system. Vinylsilane (35.0 millimoles) was circulated over mercury and irradiated for 4.5 hours. The trap in the system was kept at a temperature between -10 and $-20°$ during this period. The solid appeared after about 15 minutes, and the mercury lamp was moved several times during the experiment in order to expose clean surfaces of the tube to the radiation. Distillation of the volatile product gave 26.51 millimoles of unreacted vinylsilane at -120 to $-99°$, 0.76 millimole of additional vinylsilane at $-78°$ and 0.422 millimole of a dimer of vinylsilane at $-43°$. The spectrum of the vinylsilane which distilled at $-78°$ contained a band at 12.5–12.7 μ not in the spectrum of pure vinylsilane; this band had the same shape as that observed in the spectrum of the impure 1,2-disilylethane isolated from the silane–vinylsilane reaction.

The dimer was fractionated by condensation at $-69°$, followed by a distillation at $-52°$. At 0, 27.7 and 36.7°, its vapor pressures were 16.2, 56.5 and 65.7 mm., respectively. Its molecular weight was 112 (calcd. for $C_4H_{12}Si_2$, 116.3), and hydrolyses gave 4.80 and 4.98 moles of hydrogen evolved per mole. Of particular significance in its infrared spectrum were bands at 3.25, 3.75 and 6.2 μ, characteristic of the vinyl group, and bands at 3.42 and 6.8 μ, which indicated the presence of hydrogen bonded to saturated carbon atoms.[11] On the basis of this information and the more direct experimental evidence, there appeared to be two reasonable structures for this compound: (2-silylethyl)-vinylsilane and 1-ethyl-2-vinyldisilane.

A 0.0105-g. sample of the white solid heated to 40–60° with alcoholic KOH for several days gave 2.08 moles of hydrogen per gram atom of silicon, indicating again that the solid was polyvinylsilane.

Anal. Calcd. for $(C_2H_6Si)_x$: C, 41.32; H, 10.41; Si, 48.27. Found: C, 40.79; H, 10.21; Si, 44.87; sum, 95.87.

Discussion

Thermal Reaction of Silane and Ethylene.—Under the described conditions, the principal products at 450–510° are ethylsilane, diethylsilane and smaller quantities of disilane, trisilane and a compound tentatively identified as ethyldisilane (Table II). The formation of ethylsilane is explained readily if it is assumed that the primary step in the thermal decomposition of silane is the dissociation

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

In the presence of silane and ethylene, these reactions then can occur

$$\cdot SiH_3 + C_2H_4 \longrightarrow \cdot CH_2CH_2SiH_3$$
$$\cdot CH_2CH_2SiH_3 + SiH_4 \longrightarrow C_2H_5SiH_3 + \cdot SiH_3$$

At the temperature of the trap, $-78°$, the vapor pressure of ethylsilane is 23 mm.,[6] and thus the ethylsilane is only partially removed from the gas stream. Although ethylsilane is probably more stable thermally than silane, recirculation of ethylsilane through the heated tube may result in the breaking of a second silicon–hydrogen bond

$$C_2H_5SiH_3 \longrightarrow C_2H_5\dot{S}iH_2 + \cdot H$$

followed by

$$C_2H_5\dot{S}iH_2 + C_2H_4 \longrightarrow C_2H_5SiH_2C_2H_4\cdot$$
$$C_2H_5SiH_2C_2H_4\cdot + SiH_4 \longrightarrow (C_2H_5)_2SiH_2 + \cdot SiH_2$$

It is also possible that $C_2H_5SiH_2$ radicals are formed from

$$C_2H_5SiH_3 + \cdot H \longrightarrow C_2H_5\dot{S}iH_2 + H_2$$

In either case, diethylsilane would be formed at the expense of ethylsilane, and the amount of ethylsilane converted to diethylsilane would be expected to increase at higher temperatures. The fact that the yield of ethylsilane relative to that of diethylsilane is lower at 500–510° than at 450–475° is in accordance with this conclusion.

If the decomposition of silane does give silyl radicals, disilane may result simply by the recombination of two radicals of this type.[4] Since disilane is recirculated (its vapor pressure is 28 mm. at $-78.5°$[14]), trisilane probably is formed by the decomposition of disilane.[15] As expected, the percentage of the higher silanes in the product is greater at the lower temperatures and when the silane concentration in the reactants is raised from 20 to 50 mole per cent.

Ethyldisilane could result by either of the following mechanisms

$$C_2H_5\dot{S}iH_2 + \cdot SiH_3 \longrightarrow C_2H_5SiH_2SiH_3$$

or

$$\cdot H + Si_2H_6 \longrightarrow \cdot Si_2H_5 + H_2$$
$$\cdot Si_2H_5 + C_2H_4 \longrightarrow \cdot CH_2CH_2Si_2H_5$$
$$\cdot CH_2CH_2Si_2H_5 + SiH_4 \longrightarrow C_2H_5Si_2H_5 + \cdot SiH_3$$

When the trap in the system is not cooled, the products are passed through the heated tube repeatedly. As a result, disilane, trisilane and the compound believed to be ethyldisilane are decomposed, and the ratio of ethylsilane to diethylsilane in the product is smaller. If diethylsilane is formed by the further reaction of ethylsilane, then the latter result can be explained only by assuming that diethylsilane is less reactive than ethylsilane under these conditions, and that the formation of triethylsilane, for example, from diethylsilane proceeds at a slower rate.

Thermal Reaction of Silane and Acetylene.—Only a relatively small amount of vinylsilane resulted from the reaction of silane and acetylene at 460–510°, but compounds containing ethynyl groups attached to silicon also were formed, and the compound isolated in greatest yield was ethynyldivinylsilane (Table III).

It is probable that one of the initial products of the reaction is vinylsilane, which may result from

$$\cdot SiH_3 + C_2H_2 \longrightarrow CH{=\!=}CH\dot{S}iH_3$$
$$CH{=\!=}CH\dot{S}iH_3 + SiH_4 \longrightarrow CH_2{=\!=}CHSiH_3 + \cdot SiH_3$$

The low yield of vinylsilane means that the rates of these steps are slow or that vinylsilane at 460–510° undergoes further reaction in some way.

It is difficult to account for the formation of the ethynylsilanes by any free-radical mechanism. Possibly vinylsilanes are formed initially and then dehydrogenated, or there may be a bimolecular

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(14) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(15) K. Stokland, *Trans. Faraday Soc.*, **44**, 545 (1948); H. J. Emeleus and C. Reid, *J. Chem. Soc.*, 1021 (1939).

reaction between acetylene and silane (or between acetylene and a vinylsilane). The latter possibility is not unlikely if the acidic nature of acetylenic hydrogen and the negative character of hydrogen bonded to silicon are considered. A complex may be formed in which a center of high electron density in an acetylene molecule is coördinated with the electropositive silicon. An ethynylsilane would then result if two hydrogen atoms were eliminated, one from the silicon and one from the acetylene.

Photosensitized Reactions of Silane.—When a mixture of silane and ethylene in a flow system is irradiated at room temperature with a mercury-vapor discharge, ethylsilane, *n*-butylsilane and 1,4-disilylbutane are formed (Table IV). Acetylene and disilane are found in trace amounts. Although acetylene is formed when ethylene alone is irradiated,[16] the small quantity obtained with silane and ethylene indicates that the initial reaction in this case involves the decomposition of silane. Since all of the alkylsilanes produced contain silyl groups, it is concluded that the mercury-photosensitized decomposition of silane proceeds by the primary step

$$SiH_4 + Hg(^3P_1) \longrightarrow \cdot SiH_3 + \cdot H + Hg(^1S_0)$$

The following mechanism then is suggested for the formation of ethylsilane, *n*-butylsilane and 1,4-disilylbutane

$$\cdot SiH_3 + C_2H_4 \longrightarrow \cdot C_2H_4SiH_3$$
$$\cdot C_2H_4SiH_3 + SiH_4 \longrightarrow C_2H_5SiH_3 + \cdot SiH_3$$

and

$$\cdot C_2H_4SiH_3 + C_2H_4 \longrightarrow \cdot C_2H_4C_2H_4SiH_3$$
$$\cdot C_2H_4C_2H_4SiH_3 + SiH_4 \longrightarrow C_4H_9SiH_3 + \cdot SiH_3$$
$$2 \cdot C_2H_4SiH_3 \longrightarrow H_3SiC_4H_8SiH_3$$

If this mechanism is correct, then the silylethyl radicals, $C_2H_4SiH_3$, must react more rapidly with ethylene than with silane at room temperature, since more *n*-butylsilane is formed than ethylsilane (with an equimolar mixture of silane and ethylene). However, 1,4-disilylbutane is obtained in about the same yield as ethylsilane, and therefore the rates of both these steps must be slow if 1,4-disilylbutane is formed by recombination of two silylethyl radicals.

The absence of any 1,2-disilylethane, which would be the product from

$$\cdot SiH_3 + \cdot C_2H_4SiH_3 \longrightarrow H_3SiC_2H_4SiH_3$$

is understandable if the silyl radical is considered to react rapidly with ethylene so that its concentration is low. In turn, the quantity of disilane formed from the recombination of silyl radicals should be small, and this is found to be the case.

At least one objection can be raised to the above mechanism. If the silylethyl radicals react more rapidly with ethylene than with silane at room temperature, there is no apparent reason why the butyl radical should not act similarly: thus

$$\cdot C_2H_4C_2H_4SiH_3 + C_2H_4 \longrightarrow \cdot C_2H_4C_2H_4C_2H_4SiH_3$$

should be more rapid than

$$\cdot C_2H_4C_2H_4SiH_3 + SiH_4 \longrightarrow C_4H_9SiH_3 + \cdot SiH_3$$

However, hydrogen atoms are formed in the photosensitized decomposition, and although many probably react with silane to form hydrogen molecules and silyl radicals, the following steps also are possible

$$\cdot H + C_2H_4 \longrightarrow \cdot C_2H_5$$
$$\cdot C_2H_5 + \cdot C_2H_5 \longrightarrow C_4H_{10}$$
$$\cdot C_2H_5 + \cdot C_2H_4SiH_3 \longrightarrow C_4H_9SiH_3$$

The last reaction may be partially responsible for the high yield of *n*-butylsilane. No butane is detected in the product, however.

Presumably the formation of vinylsilane from silane and acetylene in the photosensitized reaction (Table V) proceeds by a mechanism identical with that proposed to account for its formation when the two gases are heated, except that in this instance the initial dissociation of silane is photochemical. The fact that a mirror of silicon is deposited when silane and acetylene are used, and not when silane and ethylene are irradiated, suggests that the silyl radicals do not react as rapidly with acetylene as with ethylene.

The photosensitized reaction of silane and vinylsilane yields 1,2-disilylethane, which may result from the sequence

$$\cdot SiH_3 + CH_2{=}CHSiH_3 \longrightarrow H_3SiCH_2\dot{C}HSiH_3$$
$$H_3SiCH_2CHSiH_3 + SiH_4 \longrightarrow H_3SiC_2H_4SiH_3 + \cdot SiH_3$$

However, the same solid polymeric material is formed which is produced when vinylsilane alone is irradiated, and so the above steps must compete with a second reaction, the polymerization of vinylsilane.

Photosensitized Polymerization of Vinylsilane.—The chemical properties of the polymer show that the repeating structure is $[-CH_2CH_2SiH_2-]$, in which every silicon atom is bonded to two carbon atoms. A reasonable mechanism for its formation depends on internal migrations of hydrogen atoms from silicon to carbon.

$$CH_2{=}CHSiH_3 + Hg(^3P_1) \longrightarrow CH_2{=}CH\dot{S}iH_2 + \cdot H + Hg(^1S_0)$$
$$CH_2{=}CH\dot{S}iH_2 + CH_2{=}CHSiH_3 \longrightarrow CH_2{=}CHSiH_2CH_2\dot{C}HSiH_3$$
$$CH_2{=}CHSiH_2CH_2\dot{C}HSiH_3 \longrightarrow CH_2{=}CHSiH_2CH_2CH_2\dot{S}iH_2, \text{ etc}$$

Some volatile products also are formed in the polymerization, and the compound isolated in greatest yield appears to have one of two possible structures: $CH_2{=}CHSiH_2CH_2CH_2SiH_3$ or $CH_2{=}CHSiH_2SiH_2CH_2CH_3$. The argument just presented for the polymerization supports the first structure, *i.e.*, (2-silylethyl)-vinylsilane.

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[16] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 155–164.