Radiation Induced Reaction of Silicon Hydride

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(Received May 10, 1962)

Several publications have disclosed the addition of silicon hydrides to a number of alkenes with activated peroxide or under ultraviolet light. White and Rochow¹⁾ obtained ethyl-, diethyl-, and triethylsilane by exposing a mixture of silane and ethylene to mercury vapor discharge. They indicated that the initial reaction is the decomposition of silane from the major amounts of products obtained by the irradiation of the mixture of silane and ethylene with mercury discharge in a flow system, and then concluded that the initial step involved must be the formation of hydrogen atom and silyl(SiH_3-) radical from silane. Fritz²⁾ also gave the mechanism in which the addition of the silicon hydrides to alkenes is free radical chain reaction. However, the exact course of the addition could not be determined, since further reactions of the initial products were extensive under these conditions.

The present investigation differs primarily from the above work in that the reaction was carried out at room temperature using gamma rays from 3.8 kilocurie ^{60}Co source.

No direct studies of the radiation chemistry of pure silane have been reported. The results of irradiation of pure silane and that with water, carbon dioxide and acetylene will be investigated.

Experimental

Reagents.—The reaction of silicon tetrachloride with lithium tri-*tert*-butoxaluminohydride was used for the preparation of silane³⁾. In this case the reaction was carried out in a 500 ml. flask with flow of dry nitrogen. Commercially available carbon dioxide was purified by fractional distillation at low

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

2) G. Fritz, *Z. Naturforsch.*, **7b** 507 (1952).

3) S. Sujishi and J. Kieth, *J. Am. Chem. Soc.*, **80**, 4138 (1958).

temperature. Acetylene was made from the reaction of carbide and water, and was purified by repeated distillations.

Reaction Vessel.—The vessel in which the gaseous irradiations were carried out was consisted of pyrex tube of 16 mm. outside diameter and 22 mm. length, and equipped with a breakoff seal.

Analysis of Products.—Separation of products was achieved by a serial fractional distillations and condensations following the known procedure[4]. The yield of each fraction was measured by observing the pressure exerted when the entire fraction was vaporized into a calibration column. Vapor pressure at below room temperature was measured by the conventional method. The molecular weight of each product was calculated from its vapor density. Gamma field intensity was determined by the ferrous sulfate dosimeter.

Results and Discussion

Radiation Induced Reaction of Pure Silane.—The results of the irradiation of pure silane at different pressures and radiation doses are shown in Tables I and II. In these experiments, the separation of the products was achieved by taking the advantage of the different volatilities of the products; unreacted silane was distilled at −160°C, and di- and higher silanes at −111.8 and −45°C. The noncondensable gas at 196°C was introduced into a calibrated column with a Toepler pump. Higher silicon hydrides data are not shown in the following tables because of the low concentrations and the poor precision in their analyses.

In all of the reactions, the rate of hydrogen formation did decrease with the total radiation dose and the original silane pressure increased. In each experiment, a thin layer of light brown amorphous solid deposited on the wall of the reaction vessel. It was a polymeric compound having an empirical formula $(SiH_2)_x$, which was identified by measuirng the amounts of hydrogen and silicon after decomposing the solid by heating in an incinerator.

Under the described conditions, it is assumed that SiH_3, SiH_2, Si_2H_5 and H radicals or ions are formed in the irradiation of silane. These results when plotted as a function of initial silane pressure (Fig. 1) show that the rate of hydrogen formation in irradiation decreases with increasing silane pressure. At high pressure of gas the dependence of the energy absorption upon the pressure is not linear with density. This will acount for at least a part of the effect of pressure upon $G(H_2)$: i.e. Table I.

However, this relation will depend upon the composition and the geometry of the reaction vessel and the pressure of the gas in a

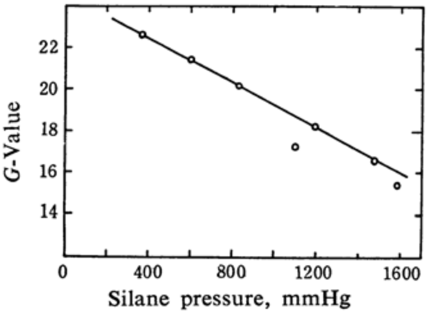

Fig. 1. Pressure dependence of hydrogen formation on the radiolysis of silane.

TABLE I. PRESSURE EFFECT ON THE RADIOLYSIS OF SILANE*

SiH_4 Pressure mmHg	Products, mmol. $\times 10^3$ H_2	$G(H_2)$	Si_2H_6	Higher silanes
380	3.19	22.8	1.27	Trace
600	4.66	21.7	1.57	Trace
820	6.13	20.5	1.56	Trace
1·100	6.88	17.2	1.33	Trace
1200	7.92	18.3	0.93	Trace
1480	8.98	16.8	1.47	None
1580	9.02	15.8	1.95	None

* Total dose was 5.81×10^{20}eV./g. for each experiment.

TABLE II. RADIATION DOSE EFFECT ON THE RADIOLYSIS OF SILANE AT 380 mmHg PRESSURE*

	Irradiation time, hr.							
Product	2	4	6.5	7.8	10	12.8	16	20.3
H_2, mmol. $\times 10^3$	1.27	1.34	1.32	1.75	1.88	2.15	2.51	3.14
$G(H_2)$	42.3	38.2	31.1	32.6	27.6	24.3	23.1	22.8

* Radiation dose rate was 2.87×10^{19}eV./g./hr.

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[4] R. T. Sanderson, "Vacuum Manipulation of Volatile Compound", John Wiley and Sons. Inc., New York, N. Y. (1948).

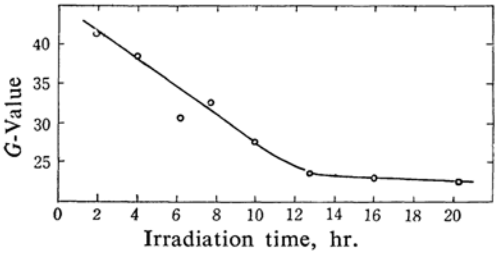

Fig. 2. Hydrogen formation as function of energy absorbed on radiolysis of silane.

complicated manner. Figure 2 shows that the rate of hydrogen formation at the low pressure (in these experimental range) decreases with irradiation time. These trend seems to favor the radical-radical reaction rather than ion-molecule reaction.

These facts suggest that unimolecular decomposition of silane might be considerd as taking place initially in two ways.

$$SiH_4 \rightsquigarrow SiH_2 + H_2 \qquad (1)$$

$$SiH_4 \rightsquigarrow \cdot SiH_3 + H \qquad (2)$$

There is no definite evidence as to which is primary reaction. But the energy of dissociation of reaction 1 very probably is not greater than the activation energy. On the other hand, the energy of dissociation for reaction 2 should be considerably greater than that of the activation. Hogness, Wilson and Johnson[5] have concluded that silylene radical is the primary product in the decomposition of silane. If this is the case, silyl radical becomes the secondary product arising from reaction such as

$$SiH_2 + SiH_4 \rightarrow 2 \cdot SiH_3 \qquad (3)$$

In this case some of SiH_2 radical loses its energy and forms polymeric solid: $(SiH_2)_x$. The formation of hydrogen produced by radical process is probably due to the reaction; the primary process may be proposed as the reaction 1 and then 3, which is followed by the following chain propagating processes;

$$\cdot SiH_3 + SiH_4 \rightarrow Si_2H_6 + \cdot H \qquad (4)$$

$$\cdot SiH_3 + Si_2H_6 \rightarrow Si_3H_8 + \cdot H \qquad (5)$$

and chain ending processes

$$2H\cdot \rightarrow H_2 \qquad (6)$$

$$2 \cdot SiH_3 \rightarrow Si_2H_6 \qquad (7)$$

Radiation Induced Reaction of Silane with Carbon Dioxide, Water and Acetylene.—Mixtures of silane and carbon dioxide were sealed into the reaction vessels in various ratios. The results of four experiments were given in Table III, only for the hydrogen formation. Analysis of the material volatile at room temperature showed the presence of silane, disilane and higher silanes in addition to the bulk of non-condensable hydrogen at −196°C. Here again a thin layer of light brown solid deposited on the wall of the reaction vessel.

TABLE III. RADIOLYSIS OF SILANE-CARBON DIOXIDE MIXTURES*

SiH_4 mmol.	CO_2 mmol.	Ratio CO_2/SiH_4	Product, H_2 mmol. $\times 10^3$	$G(H_2)$
0.455	0.		3.19	22.8
0.450	0.129	0.29	3.57	25.7
0.480	0.478	1.0	9.24	65.3
0.136	0.443	3.2	3.57	84.8

* Total dose for these experiments was 5.81×10^{20} eV./g.

The result from the radiolysis of silane with water are shown in Table IV. In case of radiolysis of a mixture of silane and acetylene, the observed G-value for the formation of hydrogen was 52.7.

TABLE IV. RADIOLYSIS ON THE MIXTURE OF SILANE AND WATER*

SiH_4 mmol.	H_2O mmol.	Product, H_2 mmol. $\times 10^3$	$G(H_2)$
0.482	3.2	17.7	119
0.487	0.005	11.1	77
0.482	0.003	7.72	52
0.422	trace	4.78	37

* Total dose was 5.81×10^{20} eV./g. in each experiment.

Striking difference was observed in the amounts of hydrogen in the radiolysis of mixiures of silane and carbon dioxide from that of pure silane even when the silane pressure and radiation dose were similar in those experiments. The increase in the G-value with carbon dioxide concentration seems to suggest that original energy absorbed by carbon dioxide somehow transfers to the silane, be it the transfer of charge or of excitation. Such transfer manifests itself as an increase in the rate of silane conversion. This effect has been noted previously in the radiolysis of acetylene[6-8], butadiene, and several inorganic gases[6].

In case of water-silane mixtures, in view of the very little reactivity of silicon hydrides toward pure water[9], the observed G-value of

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[5] T. R. Hogness, T. L. Wilson and W. C. Johnson, *J. Am. Chem. Soc.*, **58**, 108 (1936).

[6] S. C. Lind and D. C. Bardwell, ibid., **48**, 1575 (1926).

[7] R. C. Palmer and D. C. Badwell, Presented at the 134th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

[8] L. M. Dorfman and A. C. Wahl, *Radiation Research*, **10**, 680 (1956).

[9] H. J. Emeleus and J. S. Anderson, "Modern Aspect of Inorganic Chemistry", 2nd Ed., Van Norstand (1952), p. 283.

hydrogen formation was extremely high as compared to that of pure silane radiolysis. The observed results is very interesting. Energy transfer from water to silane cannot be attributed as the amounts of water used was less than one per cent. One possibility would be that the excited water molecule will abstract hydrogen atom from silane by short chain reaction, but little is known about what happens to the resulting radical in the gaseous medium. The exact nature of the chain reactions is not clear.

By comparion with a simple charge transfer reaction in the radiolysis of silane-carbon dioxide system, charge transfer reaction is not possible in the radiolysis of silane-acetylene mixtures because acetylene have a lower ionization potential than that of silane. In this system, charge transfer producing chemical changes has been known to be supressed[10]. Perhaps, the compound containing vinyl group attached to the silicon might be formed by the following reactions[1].

$$\cdot SiH_3 + C_2H_2 \rightarrow \dot{C}H{=}CHSiH_3 \qquad (8)$$

$$\dot{C}H{=}CHSiH_3 + SiH_4 \rightarrow CH_2{=}CHSiH_3 + \cdot SiH_3 \qquad (9)$$

Summary

Silane, at various pressures, has been irradiated with 3.8 kilocuries gamma rays. In all experiments, gaseous products of the reaction were hydrogen, disilane and higher silanes, while G-value for the formation of hydrogen depends on initial silane pressure and total dose. Some polymeric material with the approximate empirical formula of $(SiH_2)_x$ is also formed.

Mixtures of silane with carbon dioxide, water and acetylene were also irradiated with gamma rays, and the rate of hydrogen formation was found to increase with increasing carbon dioxide and water. This was explained by a charge transfer mechanism.

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[10] P. S. Rudolph and C. E. Melton, *J. Chem. Phys.*, 32, 586 (1960).