220. *The Pyrolysis of Disilane and Trisilane.*

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An analytical and kinetic study has been made of the thermal decomposition of disilane and trisilane on a silicon-coated glass surface, at 314—360° and 303—350°, respectively. In each case, the products are monosilane, hydrogen, silicon, and a small amount of solid hydride. Both reactions are approximately unimolecular, but show an induction period. Packing of the reaction vessel causes some retardation. Addition of hydrogen eliminates the induction period, and raises the proportion of monosilane produced, but slightly retards the reaction. If the pyrolysis of disilane is carried out in the presence of ethylene, approximately one mol. of ethylene is polymerised for every mol. of disilane decomposed, and some ethane is also formed. Trisilane polymerises about 1·3 mols. of ethylene, but more ethane is produced than in the case of disilane. These polymerisation reactions, and the effect of hydrogen in increasing the proportion of monosilane formed in the pyrolysis, are interpreted as evidence that these two reactions involve free silyl radicals.

IT was established by Stock and Somieski (*Ber.*, 1916, **49**, 111) that monosilane is decomposed thermally at about 420° into silicon and hydrogen, and more recently, Hogness, Johnson, and Wilson (*J. Amer. Chem. Soc.*, 1936, **58**, 108) have made a kinetic study of this reaction. It was found to be homogeneous, obeying a unimolecular law, and was retarded in the later stages by the hydrogen produced. Apart from a qualitative statement by Stock and

Somieski (*Ber.*, 1922, **55**, 3961) that disilane decomposes at about 300° to give monosilane as the principal product, with a little higher hydride, no observations have been made on the higher hydrides of silicon.

These reactions are of interest, not only because of the analogy they afford with the pyrolysis of hydrocarbons, but also because they may be expected to throw some light on the question of the existence of free radicals containing silicon. A specially interesting feature of the chemistry of silicon is the fact that no volatile silicon analogue of ethylene exists, and our studies in this field may, it is hoped, help to elucidate this point, as well as the analogy between the silyl and the methyl radical.

EXPERIMENTAL.

Mixed silicon hydrides were prepared by the method of Stock and Somieski (*loc. cit.*, 1916). The magnesium silicide used was, however, prepared by heating together pure magnesium filings and silicon at 620—650° for 24 hours in a stream of hydrogen. Silicide so prepared gave yields of hydrides containing up to 35% of the silicon used. The mixed hydrides were subjected to vacuum fractionation and obtained tensimetrically pure. The kinetic studies were carried out in a cylindrical, soft-glass bulb (3 cm. internal diameter) covered with a deposit of silicon. On clean glass, the reaction rate was little different, but the induction period varied considerably. With a deposit of silicon, reproducible rates were obtained in all the cases studied. The reaction bulb was connected to a capillary manometer, and by capillary taps to storage reservoirs, a Töpler pump, and the vacuum line. The reactant was introduced into the heated vessel from an auxiliary reservoir of known volume, connected with a manometer. The change in pressure recorded by the latter enabled the initial pressure of the substance undergoing pyrolysis to be calculated. The induction period in the pyrolysis enabled this initial pressure to be checked directly.

At the termination of an experiment, the reaction products were frozen out in traps cooled in liquid nitrogen and placed between the reaction vessel and the Töpler pump. The hydrogen produced was then pumped off, measured, and the residual gases analysed. Mixtures of disilane and monosilane could be separated by a single distillation at — 150° to — 160° (this temperature was obtained by means of a pentane bath). By pumping for at least one hour between these temperatures monosilane was completely removed, as was shown by tests on artificial mixtures. Thus a mixture of 38·8 c.c. of mono- and 10·3 c.c. of di-silane was prepared, and so fractionated. The volumes of gas recovered were 38·6 c.c. and 10·4 c.c. respectively. Tri- and mono-silane were separated similarly. Volume measurements were carried out in a calibrated bulb with a manometer, attached to the main vacuum apparatus. All volumes recorded are reduced to *S.T.P.*

The Pyrolysis of Disilane.—In preliminary experiments it was found that disilane commences to decompose at about 300—310°. The rate is conveniently measurable between 315° and 360°. Under the same conditions, it was verified that the decomposition of monosilane is appreciable only above 370°. The decomposition of disilane is accompanied by an increase in the total pressure, and, in order to verify that this increase is, at any instant, a true measure of the amount of decomposition, a series of experiments were carried to various stages of completion, and the amount of monosilane and hydrogen produced, and unchanged disilane, were determined by analysis. The close relationship between the silane decomposed and the pressure change is shown by the data in Table I, obtained at 314° and an initial pressure of 201 mm.

TABLE I.

Correlation of Amount of Disilane decomposed with Volume Change.

Time, hrs.	Si_2H_6, c.c.	Products (c.c.).			$\frac{Si_2H_6 \text{ decomp.}}{\text{Total } Si_2H_6}$.	$\frac{\text{Vol. change}}{\text{Total vol. change}}$.
		H_2.	SiH_4.	Si_2H_6.		
1	8·70	1·65	3·96	5·31	0·394	0·412
2	8·75	2·31	5·80	3·65	0·583	0·573
3	8·70	2·86	7·00	2·55	0·710	0·698
4	8·77	3·18	7·90	1·85	0·790	0·795
6	8·75	3·68	8·65	1·15	0·880	0·900
24	8·75	4·10	9·90	—	—	—

It will be seen that there is a reasonable agreement in the last two columns, and this justifies the use of the pressure change in a constant-volume system as a measure of the amount of disilane decomposed. It was also verified that the nature of the reaction products is independent of whether or not the bulb is packed, and is the same at 314°, 332°, 349°, and 360°.

Above 370°, however, the rate of decomposition of monosilane becomes appreciable, and this sets an upper limit to the temperature range over which the reaction may usefully be studied. In Table II are given analytical data obtained in a series of experiments in which the reaction was allowed to go to completion. They indicate that its course may be represented by the equation :

$$\underset{1\text{ mol.}}{Si_2H_6} = \underset{1\cdot10\text{ mols.}}{SiH_4} + \underset{0\cdot46\text{ mol.}}{H_2} + \underset{0\cdot90\text{ mol.}}{Si}$$

The solid deposited in the bulb is brownish-black, and it will be seen from the above equation that it still contains some hydrogen (its apparent composition is $SiH_{0\cdot7}$). In view of the experiments of Hogness, Johnson, and Wilson (*loc. cit.*), which show that hydrogen is not appreciably adsorbed by silicon, this hydrogen is probably present as the yellow polymeric hydride $(SiH_2)_x$, which has been reported from various sources. It is notable that the reaction always gives more than one molecule of monosilane per molecule of disilane decomposed. It will be seen later that the effect of added hydrogen is to increase further the proportion of monosilane, and it is therefore clear that the hydrogen found in the simple pyrolysis of disilane must also influence the nature of the products. This may be the cause of the formation of more than one molecule of monosilane.

TABLE II.

Temp.	Si_2H_6, c.c., initial.	P_{initial}, cm. Hg.	Products (c.c.). H_2.	Si_2H_6.	SiH_4.	$\frac{SiH_4}{Si_2H_6}$.	$\frac{H_2}{Si_2H_6}$.
332°	6·51	13·70	2·70	0·5	6·80	1·125	0·448
332	11·81	22·85	4·90	1·4	11·60	1·11	0·470
332	16·87	33·95	7·02	1·9	16·70	1·12	0·470
349	14·50	22·30	6·17	0·2	15·80	1·105	0·433
349	19·00	29·30	8·40	0·3	20·20	1·08	0·450
349	24·60	37·90	10·30	0·4	26·80	1·11	0·427
360	9·26	14·30	4·30	0·2	10·30	1·14	0·474
360	16·85	26·00	7·60	0·3	18·40	1·10	0·460
360	18·75	28·90	8·70	0·3	20·20	1·09	0·468

Kinetics of the Decomposition.—The rate of decomposition of disilane was determined by pressure measurements. The reaction was found to be characterised by an induction period which was of the order of six minutes at 332° but decreased at higher temperatures. The reaction was approximately of the first order, as is shown by the graph in Fig. 1, in which $\log (p_f - p_0)/(p_f - p_t)$ is plotted against the time (p_0 = initial pressure; p_f = final pressure; p_t = pressure at time t).

Reaction rates were reproducible, and for each temperature independent runs at different initial pressures were made. In Fig. 1, data obtained at 332°, 349°, and 360° are plotted and illustrate the approximately unimolecular character of the reaction. A possible clue to the significance of the induction period is given by the effect of added hydrogen (see below), which completely eliminates the initial retardation. The slight curvature at the end of the reaction is believed to be due to the effect of the hydrogen produced. The reaction is probably not homogeneous, for, as shown below, the effect of packing the reaction vessel is to retard the reaction somewhat. This finds a general explanation if the pyrolysis is assumed to be a chain reaction.

Values of the velocity constant obtained at four different temperatures are tabulated below :

T° K.	587	605	622	633
k	0·006	0·025	0·067	0·167

From these data, a graph of $\log_e k$ against $1/T$ gave a straight line, showing that over this temperature range we are dealing, in all probability, with a single reaction. The energy of activation derived from this graph is 51,300 cals., a value only a little less than that found by Hogness, Johnson, and Wilson (*loc. cit.*) for monosilane, *viz.*, 51,700 cals.

The effect of hydrogen. The effect of added hydrogen on the kinetics of the pyrolysis was studied by preparing a series of disilane–hydrogen mixtures manometrically, in the auxiliary reservoir. The effect of hydrogen was two-fold. First, it affected the rate of the reaction: by completely removing the induction period, it appeared to accelerate the reaction in its earlier stages; later, however, this was replaced by a slight retardation. Secondly, addition of hydrogen altered the ratio of the products of the reaction. The effect of hydrogen on the rate is illustrated in Fig. 2, the data for which were obtained at 332°. Here, the time is plotted against the fractional increase in pressure. The lower curve is a simple decomposition curve for 332°, and the upper one is for a mixture of disilane and hydrogen containing 48·8% of the latter. The effect of hydrogen on the later stages of the reaction may be represented by an expression of the form $k = [Si_2H_6]/[H_2]^n$, where $n = 0{\cdot}25$—$0{\cdot}35$.

FIG. 1.

Graphs illustrating the unimolecular character of the decomposition of disilane.

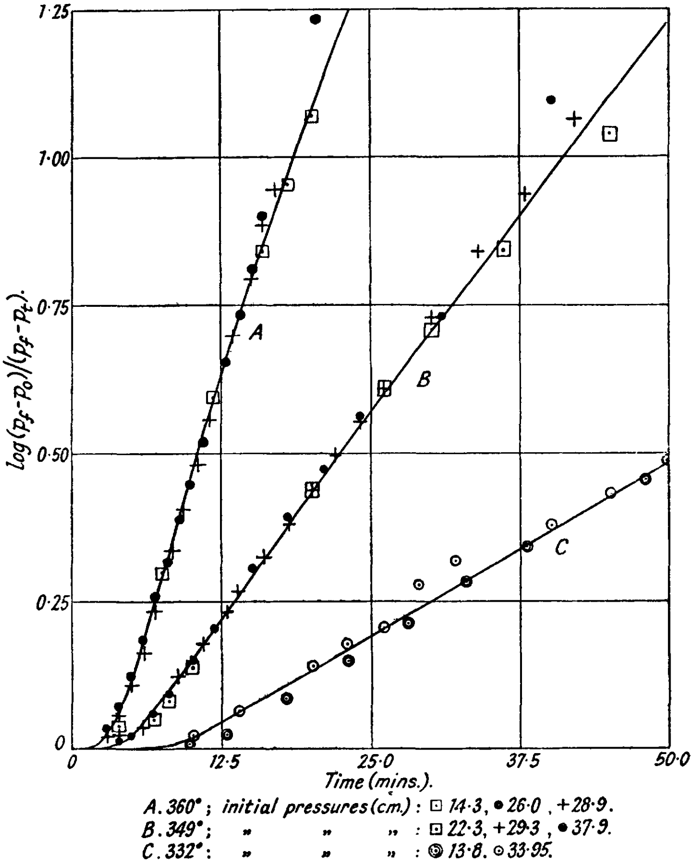


Table III shows that in the presence of excess hydrogen, the ratio

$$(SiH_4 \text{ produced})/(Si_2H_6 \text{ decomposed})$$

approaches the value 1·5. The hydrogen concentration here is much more than the total concentration at the end of the simple pyrolysis of disilane, and comparison of runs C and E shows no sensible increase in the amount of silane formed for a nine-fold increase in the amount of hydrogen. The increase in silane formed is offset by a decrease in the amount of hydrogen retained by the solid deposit. In the absence of added hydrogen (Table II) this amounts to about 10% of the hydrogen present in the disilane, whereas in the above experiments about 99% of the hydrogen remained in the gaseous phase (*i.e.*, as hydrogen or monosilane). The actual hydrogen found over and above that added at the commencement of a run is, however, much less than in the experiments recorded in Table II.

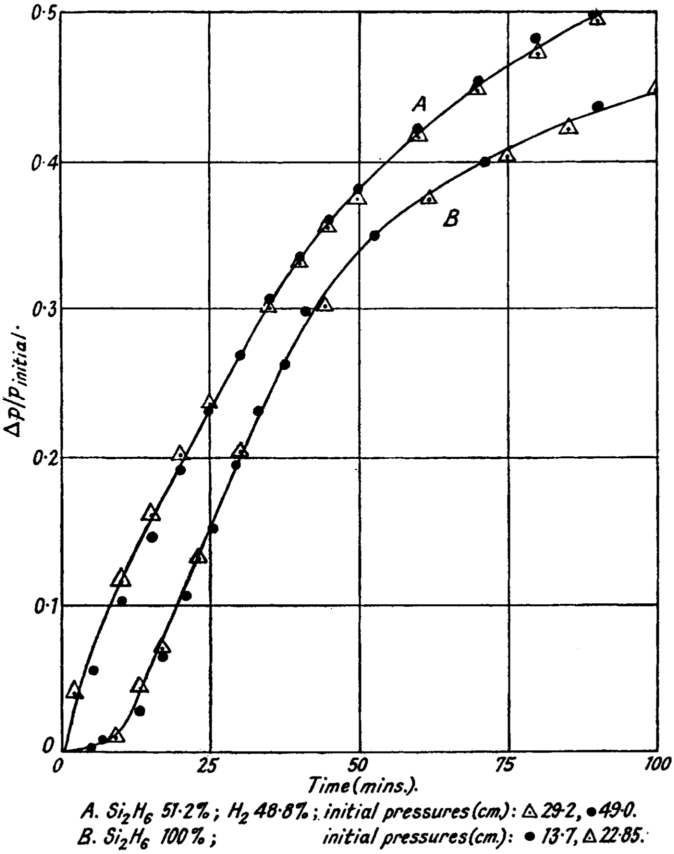
TABLE III.

Decomposition products of $Si_2H_6 + H_2$ *at* 332°.

	Si_2H_6, c.c.	H_2, c.c.	Initial pressure, cm.	SiH_4, c.c.	H_2, c.c.	$\frac{SiH_4}{Si_2H_6}$.	$\frac{H_2}{Si_2H_6}$.	H_2 in gas phase, %.	Undecomp. Si_2H_6, c.c.
A.	12·36	11·74	48·95	17·7	12·1	1·48	0·03	99·5	0·4
B.	12·41	11·79	49·00	17·4	12·3	1·46	0·043	99·3	0·5
C.	7·38	7·02	29·20	10·39	7·5	1·47	0·068	100·0	0·3
D.	7·38	7·02	29·20	10·20	7·8	1·44	0·110	99·6	0·3
E.	8·88	62·14	31·20	13·20	62·3	1·48	0·018	98·7	—
F.	5·52	38·64	19·40	8·05	38·6	1·46	nil	97·9	—

FIG. 2.

Graphs illustrating the effect of added hydrogen on the pyrolysis of disilane at 332°.



Approximately 70% *of the reaction is completed in* 70 *minutes.*

From the above analytical data, the decomposition in the presence of excess of hydrogen may be represented by the equation ·

$$\begin{array}{ccccccc} Si_2H_6 & = & SiH_4 & + & H_2 & + & Si \\ \text{1 mol.} & & \text{1·46 mols.} & & \text{0·06 mol.} & & \text{0·54 mol.} \end{array}$$

In the simple decomposition it will be remembered that 1 mol. of disilane decomposed to give only 1·12 mols. of monosilane.

The effect of packing. Packing the reaction vessel so as to give a five-fold increase in the silicon-coated glass surface was studied in the usual manner in a series of experiments at 332°.

The following results showed that a slight retardation of the reaction was produced : k is the unimolecular constant.

	A.	B.	C.	D.
$p_{Si_2H_6}$	13·7	23·1	34·0	23·4
k, unpacked	0·0245	0·0260	0·0254	0·0247
k, packed	0·0151	0·0158	0·0159	0·0153

Packing increases the half value period from 35 to 46 minutes, although this is not a very reliable indication of the effect, because of the variable induction period. The effect, although small in proportion to the increase in surface area, is clearly opposite to that which would be expected for a simple heterogeneous reaction, and this is regarded as evidence that we are dealing here with a chain reaction (see also p. 1029).

The effect of the addition of ethylene. The object of studying the effect of ethylene on this reaction was to determine if any polymerisation of the hydrocarbon took place. Taylor and Jones have shown (*J. Amer. Chem. Soc.*, 1930, **52**, 1111) that the free radicals produced by the thermal decomposition of such compounds as tetramethyl-lead at 250° will initiate a polymerisation reaction in ethylene and ethylene–hydrogen mixtures. Comparable observations in the case of the pyrolysis of disilane would, it was thought, afford some evidence of the transient existence of free silyl radicals in the reaction. This point lends itself to experimental study because disilane may be pyrolysed at a temperature well below that at which ethylene itself undergoes change. Experiments on a mixture of disilane and ethylene in various proportions showed that polymerisation did occur. In this case, pressure change cannot be used as a measure of the amount of the reaction, since there is first an increase in pressure and then a decrease. The uncertainty of the interpretation of the pressure change thus prevents a study of the effect of ethylene on the kinetics of the reaction, and the main conclusions have to be drawn from analytical data.

The mixture to be analysed at the end of a pyrolysis run in presence of ethylene may contain hydrogen, monosilane, ethylene, and ethane. Analyses were carried out by first immersing the reaction bulb in liquid nitrogen, at least 30 minutes being allowed for condensable material to separate from the hydrogen atmosphere. Hydrogen was then pumped off and measured. The residual gas was all volatile at − 140°, and thus presumably did not contain hydrocarbons other than ethane and ethylene. It was shaken with 40% sodium hydroxide solution to decompose monosilane, and the hydrogen produced pumped off and measured. The residual gas was measured, shaken with bromine-water followed by alkali, and the contraction noted. The undecomposed gas was allowed to accumulate from several runs, and finally identified tensimetrically as ethane.

Analytical data obtained in a series of experiments at 332° are shown in Table IV.

TABLE IV.

Effect of ethylene on the pyrolysis of disilane.

Si_2H_6, c.c.	C_2H_4, c.c.	$\frac{Si_2H_6}{C_2H_4}$.	Total pressure, cm.	Products (c.c.).				Calc. compn. of solid.
				SiH_4.	H_2.	C_2H_4.	C_2H_6.	
24·3	10·4	2·33	41·6	22·6	2·9	nil	3·00	$C_2H_{10}Si_{3·54}$
20·2	8·6	2·33	34·6	19·1	2·5	nil	2·00	$C_2H_{8·2}Si_{3·07}$
17·2	7·3	2·33	29·2	19·1	1·85	nil	1·85	$C_2H_{9·85}Si_{3·02}$
9·63	15·73	0·625	29·6	8·60	1·9	7·2	1·7	$C_2H_{4·4}Si_{1·13}$
11·8	23·8	0·496	42·15	10·1	2·3	6·7	5·00	$C_2H_{4·99}Si_{1·12}$
10·1	20·3	0·496	36·22	8·64	2·2	5·75	4·58	$C_2H_{4·52}Si_{1·15}$
8·1	33·7	0·247	51·75	7·00	1·4	21·73	3·80	$C_2H_{4·75}Si_{1·12}$
6·6	27·0	0·247	41·52	5·72	1·2	17·5	3·10	$C_2H_{4·95}Si_{1·14}$

From these data it will be seen that very little hydrogen is produced in the reaction, particularly when the ethylene is in excess. The amount of monosilane in the gaseous product is also considerably less than in the direct pyrolysis. The mean yield, when there is an excess of ethylene, is only 0·85 mol. of monosilane per mol. of disilane decomposed.

Approximately 1·5 mols. of ethylene per mol. of disilane is the maximum that may be decomposed under the conditions of these experiments; of this, about one-third appears as ethane, so the amount of ethylene polymerised is approximately equal to the amount of disilane decomposed. This is to be contrasted with the 6—7 mols. of ethylene polymerised by every methyl radical in the experiments of Taylor and Jones (*loc. cit.*). The hydrogen which normally appears in the pyrolysis of disilane is partly used up in the reduction of ethylene to ethane, It was shown by suitable blank experiments that this cannot occur as a heterogeneous reaction on a silicon surface at the temperature used.

The composition of the solid deposit may be calculated from the deficit of products found in the gaseous phase. This has been done in the last column of Table IV, and it is seen that, as the amount of ethylene is increased, the limiting composition of the solid approximates to C_2SiH_5. The grey-black film formed in the simple pyrolysis is entirely absent, but instead, a yellow to red resinous material appears. This solid is insoluble in water and organic solvents, but is decomposed by strong alkali, with the evolution of some hydrogen. It is believed that the silyl radicals initiating the polymerisation are actually incorporated in the polymer, but it could not be shown definitely that the solid was homogeneous.

The effect of ethylene and hydrogen. Since the presence of ethylene caused less hydrogen to appear in the decomposition products, it was of interest to examine the effect of the addition of hydrogen to the reaction mixture, as was done by Taylor and Jones. Mixtures containing a fairly large excess of hydrogen were prepared, and pyrolysed in a 250-c.c. bulb. Analyses were carried out as before, and it was found that, not only was no hydrogen produced as a result of the disilane decomposition, but a small amount of the added hydrogen disappeared. The amount of ethane found was increased considerably, as in the experiments of Taylor and Jones, and the amount of polymer deposited was less. The analytical results are summarised below :

The Effect of Hydrogen and Ethylene on the Pyrolysis of Disilane at 332°.

Si_2H_6, c.c.	C_2H_4, c.c.	H_2, c.c.	Total pressure, cm.	Products (c.c.). H_2.	SiH_4.	C_2H_4.	C_2H_6.	Compn. of solid.
7·54	16·25	31·3	24·15	30·7	7·70	7·40	6·20	$C_2H_{5\cdot3}Si_{2\cdot8}$
5·10	11·06	21·3	16·40	20·1	5·42	5·23	4·40	$C_2H_{5\cdot8}Si_{3\cdot3}$
7·65	16·50	31·6	24·45	29·9	7·83	7·62	6·45	$C_2H_{6\cdot1}Si_{3\cdot07}$
5·42	11·70	22·4	17·35	21·4	5·60	5·27	4·80	$C_2H_{5\cdot6}Si_{3\cdot22}$

Since in all these experiments there is an excess of ethylene over disilane, if the hydrogen had no effect, we should expect as before, approximately one mol. of ethylene polymerised per mol. of disilane decomposed. Instead only about 0·3 mol. is polymerised, whereas the amount of ethane increases from 0·46 to about 0·86 mol. per mol. of disilane decomposed. At the same time the amount of monosilane is increased from 0·85 mol. per mol. of disilane decomposed in the case of disilane and ethylene to 1·03 in the case of disilane, ethylene, and hydrogen mixtures.

The Pyrolysis of Trisilane.—The temperature of incipient decomposition of trisilane was found to be about 300°, *i.e.*, practically the same as for disilane. The products of the reaction were monosilane, hydrogen, and a solid product which was almost pure silicon. A very careful fractionation was carried out on the combined products of a series of experiments, in order to ascertain whether or not any disilane was formed. The result was entirely negative. As in the case of disilane, the next task was to correlate the pressure change with the amount of decomposition. This was done in a series of experiments carried out at 316°, in which the reaction was allowed to proceed for 30, 60, 90, and 120 mins. severally before condensing the products in liquid air. The results are shown below.

Correlation of Trisilane decomposed with Volume Change.

Time, hrs.	Si_3H_8, c.c.	Products (c.c.). H_2.	SiH_4.	Si_3H_8.	$\frac{Si_3H_8 \text{ decomp.}}{\text{Total } Si_3H_8}$.	$\frac{\text{Vol. change}}{\text{Total vol. change}}$.
½	26·6	7·95	13·3	17·7	0·334	0·324
1	26·8	15·0	24·1	10·7	0·600	0·596
1½	26·6	18·3	29·3	7·4	0·723	0·743
2	26·6	20·63	32·6	4·6	0·827	0·813
∞	26·6	24·1	40·5	0·2	—	—

The pyrolysis yields more hydrogen than in the case of disilane, one mol. of trisilane giving just less than one mol. of hydrogen. As more monosilane is also produced, molecule for molecule, the ratio of final to initial pressure is considerably greater in this case—2·42 as against 1·47 for disilane. The net reaction may be represented as

$$\underset{1 \text{ mol.}}{Si_3H_8} = \underset{1\cdot53 \text{ mols.}}{SiH_4} + \underset{0\cdot90 \text{ mol.}}{H_2} + \underset{1\cdot47 \text{ mols.}}{Si}$$

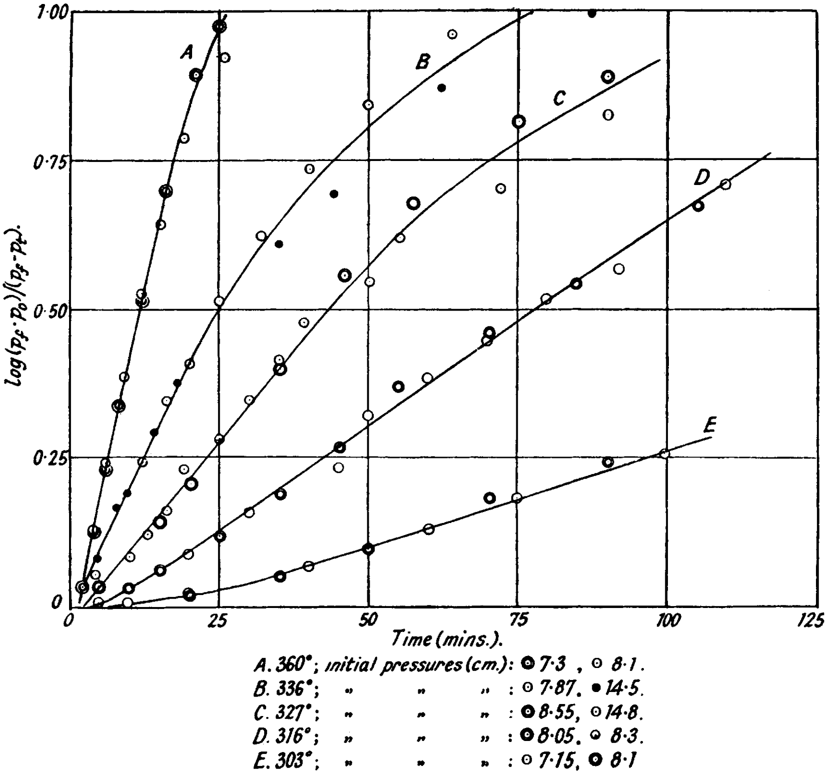
It will be seen that all the hydrogen is accounted for in the gaseous phase. The detailed analyses are given on the following page.

Pyrolysis of Trisilane at a Silicon-coated Surface.

Temp.	Initial vol., c.c.	Initial pressure, cm.	Products (c.c.). H_2.	SiH_4.	$\frac{SiH_4}{Si_3H_8}$.	$\frac{H_2}{Si_3H_8}$.
327°	34·2	14·80	30·10	52·7	1·54	0·880
327	19·7	8·55	18·05	30·2	1·53	0·915
327	16·8	7·30	15·30	25·8	1·53	0·910
336	33·0	14·50	29·20	51·0	1·55	0·885
336	18·75	8·31	17·20	29·15	1·54	0·917
336	17·95	7·87	16·00	27·6	1·53	0·891
350	29·6	13·15	26·7	44·2	1·49	0·904
350	18·25	8·10	16·10	27·9	1·52	0·882
350	16·50	7·30	15·30	24·7	1·49	0·927

Fig. 3.

Graphs illustrating the unimolecular character of the decomposition of trisilane.



Kinetics of the pyrolysis. The reaction was again studied by means of the change in pressure, and proved to be unimolecular, although the retardation towards the end was a little more pronounced than in the case of disilane. This was attributed to the greater proportion of hydrogen produced. As in the case of disilane, reaction rates were quite reproducible when measurements were made with a silicon film in the bulb. An induction period was again present, but was less than for the case of disilane. The velocity constants given below show that the reaction is a little more rapid than the decomposition of disilane at corresponding temperatures. This small difference is sufficient to make it unnecessary to investigate the reaction above 350°. Below this temperature the possibility of the decomposition of any monosilane is excluded. The logarithmic curves for the decomposition are given in Fig. 3. Attempts to fit the data to an expression for any other order were unsuccessful.

Velocity constant for the decomposition of trisilane.

Temp., ° K.	576	589	600	609	623
k	0·00667	0·0154	0·0297	0·0460	0·1150

From the data for the velocity constant, the energy of activation was found to be 43,000 cals.

The effect of hydrogen on the pyrolysis of trisilane. The effect of hydrogen was examined, exactly as for disilane. The proportion of monosilane in the reaction products is increased by the presence of hydrogen. From the analytical data given below, the limiting value appears to be 2 vols. of monosilane per mol. of trisilane; even with a large excess of hydrogen this value is not exceeded. Again the solid deposit is almost pure silicon, over 99% of the hydrogen appearing in the gaseous phase as such and as monosilane.

Pyrolysis of hydrogen plus trisilane.

Initl. $\frac{Si_3H_8}{H_2}$.	Si_3H_8, c.c.	H_2, c.c.	Initial pressure.	Products (c.c.).		$\frac{SiH_4}{Si_3H_8}$.	$\frac{H_2\text{ produced}}{Si_3H_8}$.
				H_2.	SiH_4.		
0·288	15·0	51·0	29·50	56·4	27·2	1·83	0·36
0·288	8·05	27·9	15·70	30·3	14·75	1·83	0·30
0·288	15·95	55·55	31·30	60·85	29·30	1·84	0·33
0·288	8·49	29·4	16·65	32·0	15·95	1·89	0·31
0·167	13·5	80·83	41·15	81·1	26·00	1·93	0·02
0·167	7·99	47·91	24·50	48·05	15·80	1·975	0·018
0·111	9·43	84·87	41·15	85·00	18·70	1·98	0·014

The effect of ethylene. Experiments were carried out, as in the case of disilane, in which an excess of ethylene was added to the reactant. It was found that polymerisation of the ethylene again took place. The products of the reaction were essentially the same as in the previous case, and analyses were performed in the same manner. The results are tabulated below.

Effect of ethylene on the pyrolysis of trisilane.

Si_3H_8, c.c.	C_2H_4, c.c.	$\frac{Si_3H_8}{C_2H_4}$.	Total presture, cm.	Products (c.c.).				Calc. compn. of solid.
				H_2.	SiH_4.	C_2H_4.	C_2H_6.	
16·50	42·00	0·392	25·70	2·15	21·0	10·00	10·8	$C_2Si_{1\cdot34}H_{5\cdot12}$
9·12	23·18	0·392	14·20	1·26	11·33	5·65	5·8	$C_2Si_{1\cdot37}H_{5\cdot16}$
8·78	58·50	0·150	29·49	0·70	10·70	40·95	5·45	$C_2Si_{1\cdot29}H_{5\cdot27}$

Examination of these data shows that the ratio of monosilane to trisilane in the products is lowered to 1·25 (1·53 in simple pyrolysis). The amount of ethylene polymerised is 1·33 mols. per mol. of trisilane decomposed, as against about 1·00 per mol. of disilane. The ethane produced is 0·62 mol. compared with 0·45 for disilane. The solid product is, however, not very different from that formed in the case of disilane, although the silicon content is rather higher.

DISCUSSION.

Probably the most satisfactory basis for the discussion of the mechanism of the pyrolysis of disilane is that provided by analogy with the case of ethane. The decomposition of ethane at about 580—620° is, in its initial stages at least, a homogeneous reaction of the first order. There are undoubtedly secondary reactions, however, and Travers has recently suggested that the initial stage of the reaction is heterogeneous (Faraday Society Discussion on Hydrocarbon Chemistry, 1939). The mechanism suggested by Rice, and by Rice and Herzfeld (*J. Amer. Chem. Soc.*, 1931, **53**, 1959; 1934, **56**, 284) for the decomposition of ethane involves an initial dissociation into two methyl radicals, followed by a chain reaction in which the essential chain carrier is atomic hydrogen. If a similar series of reactions is written for disilane, the following represents the main chain :

$$Si_2H_6 = 2SiH_3 \qquad (1)$$
$$SiH_3 + Si_2H_6 = SiH_4 + Si_2H_5 \qquad (2)$$
$$Si_2H_5 = SiH_4 + H \qquad (3)$$
$$H + Si_2H_6 = Si_2H_5 + H_2 \qquad (4)$$

Chain termination would then occur by interaction of the radicals concerned, or by their reaction with atomic hydrogen. The energy of activation of these reactions is at present unknown. It is also necessary to postulate that silicoethylene partly decomposes into silicon and hydrogen (with possibly some monosilane), and is to a smaller extent polymerised to $(SiH_2)_n$, which is stable thermally up to 380° (Schwartz and Heinrich, *Z. anorg. Chem.*, 1935, **221**, 272). The fact that the reaction is retarded somewhat by packing accords with such a chain mechanism. The observed effect of hydrogen in eliminating the induction period in the pyrolysis can be accounted for by supposing that the reaction

$$SiH_3 + H_2 = SiH_4 + H \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

occurs, as is indicated by the increased yield of monosilane when the reaction is carried out in the presence of added hydrogen. This reaction is probably somewhat endothermic. In the early stages of the simple decomposition, the concentration of hydrogen is very small, and the whole chain reaction may depend on such a reaction as the above if interaction between a silyl radical and disilane does not occur readily.

During the later stages the apparent retardation of the reaction by hydrogen may be due to its reaction with SiH or SiH_2 radicals, to form monosilane. This is in accordance with the retardation found by Hogness, Johnson, and Wilson (*loc. cit.*) in the pyrolysis of monosilane.

No higher hydrides could be detected in the products of the reaction at any stage, so it would appear that the interaction of radicals to form larger molecules is not an important factor in the reaction.

If the decomposition of disilane occurred according to the mechanism proposed by Kassel and Storch (*J. Amer. Chem. Soc.*, 1937, **59**, 1245) for ethane, *viz.*,

$$Si_2H_6 = Si_2H_4 + H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$
$$Si_2H_4 + Si_2H_6 = Si_4H_{10} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$
$$Si_4H_{10} = SiH_4 + Si_3H_6 \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

it would be difficult to explain the effect of hydrogen in removing the induction period. Also, it would imply a rather greater stability of silicoethylene than is indicated by the many failures to prepare this substance.

The polymerisation of ethylene, due to the decomposition of disilane, would appear to be a genuine example of induced polymerisation, and to be parallel to that observed with ethylene in the presence of methyl radicals from metal alkyls (Taylor and Jones, *loc. cit.*). In the case of the metal alkyl, however, 12 molecules of ethylene were polymerised for every molecule of metal alkyl decomposed, whereas in the case of disilane, the number is approximately unity. It would appear, therefore, that some of the other possible reactions of the silyl radicals are more favoured than that with ethylene. That silicon-containing radicals rather than hydrogen atoms are responsible for the polymerisation is indicated by the fact that considerably more silicon goes into the solid state, and less appears as monosilane. The silicon seems to be definitely combined in the polymer.

The effect of nitric oxide on the rate of the reaction, and the effect of lowering the initial pressure to less than 5 cm., are other points which are being investigated. The mechanism of the pyrolysis of trisilane is uncertain, and in view of the many possible steps, for none of which energies of activation are known, the formulation of a complete reaction scheme would be purely tentative. Certain inferences may, however, be drawn. The removal of the induction period and the enhanced yield of monosilane when the reaction is carried out in an excess of hydrogen indicate that silyl radicals again play an important part in the mechanism. The fact that the decomposition of 1 mol. of trisilane leads to the production of 1·3 mols. of polymer, as compared with approximately one in the case of disilane, indicates that more active radicals are produced from trisilane than from disilane, as might be anticipated. The fact that the maximum yield of monosilane when the reaction is carried out in excess of hydrogen is almost exactly 2 mols. per mol. of trisilane suggests that the reaction

$$Si_3H_8 = 2SiH_3 + SiH_2$$

may occur, the silyl radicals being hydrogenated to monosilane, and the silylene radical being dehydrogenated.

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