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THE THERMAL DECOMPOSITION OF DISILANE AND TRISILANE.

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In a paper on the thermal decomposition of ordinary disilane and trisilane Emeléus and Reid [1] have reported that these reactions proceed in a relatively simple manner, at any rate when compared with the results of the decomposition of the analogous hydrocarbons. (For information regarding the latter reactions see, for example, the monographs of Steacie [2] and Schumacher.[3]) Thus, in the decomposition of both the silicon hydrides mentioned above the only reaction products found at any stage were hydrogen, monosilane and silicon. This latter substance contained in the case of disilane a considerable amount of hydrogen, corresponding to an average composition $SiH_{0 \cdot 7}$, whilst in the decomposition of trisilane the deposited silicon was almost free from hydrogen. The experimental procedure was still further simplified by their discovery that the pressure

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[1] Emeléus and Reid, *J. Chem. Soc.*, 1939, 1021.

[2] Steacie, *Atomic and Free Radical Reactions* (New York, 1946).

[3] Schumacher, *Chemische Gasreaktionen* (Dresden and Leipzig, 1938)

change was very nearly proportional to the amount of decomposition for both silanes. This enabled the course of the reaction to be followed by pressure measurements, and series of experiments at different temperatures have been performed according to this method by the above-mentioned investigators.

The statement concerning the composition of the reaction mixture in the decomposition of disilane is not in agreement with the results of Stock and Somieski.[4] These investigators found that at not too high temperatures higher silanes also were formed in fairly large amounts.

The results obtained by Stock and Somieski, however, are not quite comparable with those obtained by Emeléus and Reid, since the former investigators used a dynamical method in decomposing the disilane, whilst the latter carried out their experiments under static conditions. In general, dynamical methods may often be assumed to give mixtures of reaction products somewhat different in composition from those obtained by statical methods. In this instance it seems reasonable to believe that the dynamical method used by Stock and Somieski favoured the formation of the higher silanes. In the earlier stages of the reaction there is a large probability of collision between the unchanged disilane molecules and the radicals which are presumably the first product of decomposition, and although the thermal stability of the silanes decreases with increasing molecular weight, the result of such collisions might be a certain amount of trisilane. This latter substance may then further react in a similar way to form tetrasilane and so on. By rapid cooling of the reaction mixture down to temperatures where the higher silanes are stable, larger amounts of these substances should be expected.

For the same reason it might have been expected that such compounds should also have been found, though to a lesser extent, when analysing the reaction mixture from the statical experiments. It is, of course, possible that the stationary concentration of such radicals was too small to produce higher silanes in sufficient quantity to be detectable by fractionation after quenching. However, the results from the analogous decomposition experiments with ethane make it probable that higher silanes would actually be formed in the reaction vessel.

In a series of investigations * on some properties of the lower silanes with light and heavy hydrogen, carried out by the present author, their thermal stability has been studied. Owing to the uncertainties referred to above, it was necessary to re-examine the course of the decomposition by analyses of the reaction mixture.

Experimental.

The construction of the apparatus for pyrolysis of the silanes was similar to that employed by Hogness, Wilson and Johnson [5] in research on the decomposition of monosilane, the most important difference being that in the present investigations a spherical reaction vessel was used instead of a cylindrical one as in the experiments of the authors just mentioned. The vessel had a capacity of about 250 ml. In order to obtain information as to a possible influence of the surface on the rate of decomposition two pieces of apparatus of this kind were used. In one of them (called A in the following) the reaction vessel was unpacked, whilst in the other (B) the vessel was filled with small Raschig rings, thus producing a variation in the surface-volume ratio of about 1 : 20. Both the apparatus and the Raschig rings were made of Duran glass, but before use the inner surfaces were completely covered by silicon, deposited from decomposition of some samples of monosilane.

Each apparatus was supported on the top of a large electric furnace, the reaction bulb hanging freely in the middle of it. The temperatures were measured

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[4] Stock and Somieski, *Ber.*, 1923, **56**, 247.

* To be published shortly.

[5] Hogness, Wilson and Johnson, *J. Amer. Chem. Soc.*, 1936, **58**, 108.

by means of nickel-nichrome thermocouples, the electromotive force being determined potentiometrically. The thermocouples were calibrated at the melting points of tin, lead, zinc and aluminium. The samples of the three latter metals had been furnished, together with certificates, by the National Bureau of Standards, U.S.A., whilst the sample of tin was a *pro analysi* preparation from Merck. The potentiometer, the sensitive galvanometer and the certificated standard cells used were all manufactured by Tinsley and Co.

Since the room temperature was maintained fairly constant, temperature variations were due almost entirely to variations of the voltage in the network. No automatic device was employed to compensate this effect. Instead, the current was kept as constant as possible by manual operation of a resistance in series with the furnace. As the furnace had a very large heat capacity and the experimental temperatures were comparatively low, this procedure required little experience in order to maintain the temperature within the limits of variation of ±0·1°c. Further, in order to smooth out possible temperature gradients, a thick-walled cylindrical aluminium box was inserted, the lid of which was divided into two parts and provided with holes for the thermocouple and the capillary of the reaction bulb. The preparation of the crude mixture of silanes and the separation of the individual components from it by fractionation were very carefully performed in a manner similar to that described by Stock and Somieski.[6]

Each sample of a pure substance was accurately measured in one of the calibrated sections of the large vacuum apparatus and transferred by means of liquid nitrogen into an auxiliary cylindrical vessel fitted with a tap and attached to the apparatus with a ground joint. Then the vessel was detached and connected to the decomposition apparatus. This latter was now thoroughly evacuated, and in the meantime the sample was allowed to evaporate and attain room temperature. Just before starting an experiment the manometer of the apparatus was read and simultaneously the atmospheric pressure. This was necessary because in these experiments an open manometer was used. Then the tap between the pump and the apparatus was closed and the silane allowed to stream into the apparatus until the pressures were equalised. The time necessary for this operation was 2-4 sec., and the moment of opening of the tap was taken as zero time. Immediately after closing the tap of the decomposition apparatus the pressure was read. This was always possible in these experiments on account of the apparent induction periods.

The amount of silane remaining in the auxiliary vessel and the external part of the apparatus was frozen in liquid nitrogen, transferred back into the vacuum apparatus and the volume measured. The difference between the two volume determinations was the amount taken for the decomposition.

The decomposition was now allowed to proceed for a length of time decided on beforehand. The manometer and the atmospheric pressure were again read, and immediately afterwards the reaction mixture was pumped off through a long U-tube of about 10 mm. diam. immersed in liquid nitrogen in order to condense the reaction products for analysis. This operation was carried out as rapidly as possible in order to prevent further decomposition, but not so rapidly as to pull condensable gases through the trap. The hydrogen formed was not collected, but was drawn off through the pump. This procedure was considered to be the best one since the collection of hydrogen would have required a Töpler-pump or some other slowly working device. Instead the amount of hydrogen was indirectly determined. However, even though the results so obtained seem to be very reasonable, as will appear from the following tables, it must be admitted that direct checks upon the amounts so found would have been of great value.

The condensate was brought into the large vacuum apparatus and analysed by means of fractionation at low pressures. Thus, monosilane was distilled off at about −160° c., disilane at about −105° c., trisilane at −70° c. and tetrasilane at −30° c. When a residue still remained after these distillations it was always very small in amount, and it has therefore been combined with and recorded as tetrasilane. This should cause only very small errors in the subsequent calculations. Of course, objections may be made to the method of separation of the components of the mixture ; but at the present time no better method is available for this purpose. Repeated fractionations of the same mixture in most cases showed good agreement, and the vapour pressures of the single components generally did not differ appreciably from those determined on very pure samples of the same substances.

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[6] Stock and Somieski, *Ber.*, 1916, **49**, 111.

Results.

The results of the experimental investigations are shown in Tables I and II. Owing to difficulties caused by the war situation, rather limited series of experiments have been carried out. The decomposition of disilane has been studied at five different temperatures but at one pressure only, viz. about 10 cm., whilst in the case of trisilane a single series of experiments at about 592° K. and about 8 cm. pressure has been performed.

The two tables have been arranged as follows. The first four columns show the absolute temperatures, times, reaction vessels used and apparent induction periods of the experiments. In columns 5 and 6 are listed the figures of the initial pressures and changes of pressure. The next three columns show the amounts of silane employed, recovered and decomposed given in ml. N.T.P., and the next column gives the % amounts decomposed. Then follow the relative changes of pressure expressed for convenience as $100\frac{\Delta p}{p_0}$. The amounts of hydrogen given have been calculated from the changes of pressure and the amounts of the other volatile components of the reaction mixture. The columns 13, 14 and 15 show the amounts of these latter substances, also referred to N.T.P. Finally, the last two columns give the amounts of the hydrogen-containing deposits of silicon given as ml. of the hypothetical gaseous compound SiH_x, and the value of x. These two quantities have been calculated from the differences between the amounts of silicon and hydrogen in the original sample of silane and those of the gaseous reaction products. The tables give strong evidence that in the decomposition of disilane and trisilane, higher silanes are really among the products formed.

In trying to find the correct order of reaction in the two cases the data obtained at each temperature have been plotted appropriately for different orders. The temperature variations within each series of experiments are only small and most probably cause less error than some other factors. Further, since it is a somewhat difficult matter to correct the results to a common temperature, no such corrections have been applied.

From the plots it was found that the rate of decomposition could be represented approximately only by a first-order relationship. The first-order graphs for the decomposition of disilane at about 584, 611 and 633° K. are shown in Fig. 1, 2 and 3, respectively, and for the single series of trisilane in Fig. 4. In the early stages of the decomposition there was an almost linear dependence of $\log \frac{p_0}{p_t}$ with time (p_0 = initial pressure, p_t = pressure at a time t). In the later stages, however, considerable deviations from the unimolecular course were found as is shown by the graphs. This result is quite similar to that found in the pyrolysis of the monosilane, carried out by Hogness, Wilson and Johnson and later confirmed by the present author.

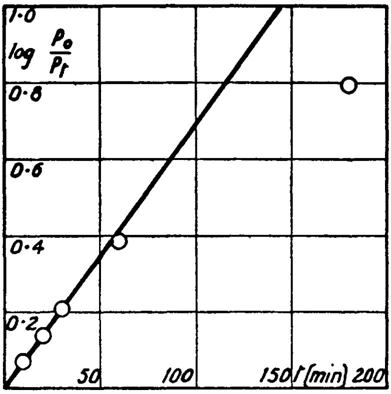

FIG. 1.

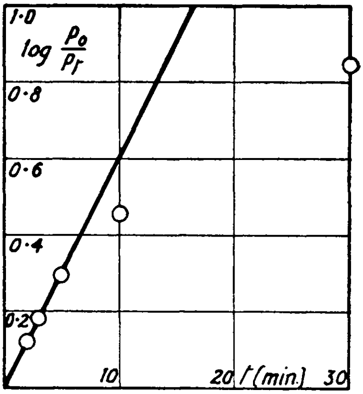

FIG. 2.

The curves seem in all cases to pass through the origin, and in the graphs only the limiting straight lines corresponding to an ideal unimolecular course

TABLE I.—THERMAL DECOMPOSITION OF Si_2H_6.

Temp.	Time.	Re-action vessel.	Apparent Induction Period.	p_0.	Δp.	Si_2H_6.				$100\frac{\Delta p}{p_0}$.	Reaction Products.					x in $(SiH_x)_n$.
						Empl.	Rec.	Dec.			H_2.	SiH_4.	Si_3H_8.	Si_4H_{10}.	SiH_x.	
°K.	min.		min.	mm.	mm.	ml.	ml.	ml.	%.		ml.	ml.	ml.	ml.	ml.	
584·6	10	A	10-15	90·5	0·1	16·30	13·86	2·44	15·0	0·1	0	1·55	1·05	0·05	0	—
584·9	20	A	—	88·0	0·7	15·78	11·47	4·31	27·3	0·8	0	2·80	1·77	0·13	0	—
584·6	30	A	—	88·3	1·2	16·19	10·00	6·19	38·2	1·4	0·22	3·86	1·93	0·39	1·17	1·64
584·5	60	A	—	88·7	7·2	15·99	6·54	9·45	59·1	8·1	0·72	7·69	1·78	0·56	3·63	1·28
584·2	180	A	—	89·8	32·5	16·06	2·58	13·48	83·9	36·2	2·31	15·93	0·78	0·27	7·61	0·47
583·7	24 hr.	A	—	90·5	61·0	16·45	0·79	15·66	95·2	67·4	6·66	19·95	0·14	0	10·95	0
597·5	3	B	5	110·0	0	14·51	12·64	1·87	12·9	0	0	1·14	0·82	0·09	0	—
597·3	5	B	—	108·8	0·4	14·32	11·43	2·89	20·2	0·4	0	2·02	1·07	0·14	0	—
611·2	2	B	3	109·7	0·7	13·93	10·57	3·36	24·1	0·6	0	2·28	1·29	0·11	0	—
611·9	3	B	—	110·8	0·6	14·14	9·33	4·81	34·0	0·5	0	3·00	1·54	0·40	0·40	1·35
611·4	5	B	—	106·9	2·1	13·70	6·96	6·74	49·2	2·0	0·21	4·67	1·62	0·51	1·91	1·72
611·5	10	B	—	108·1	10·1	13·85	4·88	8·97	64·8	9·3	0·76	7·83	1·22	0·45	4·65	1·45
611·9	30	B	—	107·4	47·8	13·63	1·95	11·68	85·7	44·5	2·95	14·08	0·54	0·18	6·94	0·25
613·1	24 hr.	B	—	107·0	108·7	13·63	0·23	13·40	98·3	101·6	14·48	12·73	0·04	0	13·95	0·01
621·2	1	A	1·5	92·3	0·5	15·63	12·44	3·19	20·4	0·5	0	2·03	1·27	0·06	0·30	0·87
621·0	2	A	—	92·0	0·9	15·69	9·92	5·77	36·8	1·0	0·43	3·43	1·89	0·18	1·72	1·81
633·4	1	A	1	93·6	0·5	15·51	10·38	5·13	33·1	0·5	0	3·56	1·68	0·13	1·14	1·58
632·7	2	A	—	93·0	6·8	15·54	6·96	8·58	55·2	7·3	0·71	6·90	1·72	0·38	3·58	1·37
633·2	3	A	—	92·4	12·2	15·46	4·70	10·76	69·6	13·2	0·67	10·43	1·27	0·43	5·56	1·27
632·7	5	A	—	92·8	24·0	15·51	3·15	12·36	79·7	25·9	1·53	13·74	0·86	0·25	7·40	0·91
632·5	24 hr.	A	—	93·0	154·2	15·64	0·01	15·63	99·9	165·8	37·38	4·14	0·04	0	27·00	0·08

TABLE II.—THERMAL DECOMPOSITION OF Si_2H_8.

Temp.	Time.	Re-action Vessel.	Apparent Induction Period.	p_0.	Δp.	Si_3H_8.				$100\frac{\Delta p}{p_0}$.	Reaction Products.					x in $(SiH_x)_n$.
						Empl.	Rec.	Dec.			H_2.	SiH_4.	Si_2H_6.	Si_4H_{10}.	SiH_x.	
°K.	min.		min.	mm.	mm.	ml.	ml.	ml.	%.		ml.	ml.	ml.	ml.	ml.	
591·5	5	A	2	74·8	1·7	13·48	10·36	3·12	23·1	2·3	1·00	2·02	0·35	0·05	6·44	1·91
591·7	10	A	—	75·0	5·3	13·57	8·43	5·14	37·9	7·1	1·28	4·08	0·57	0·16	9·56	1·80
591·8	15	A	—	75·3	10·7	13·61	6·84	6·77	49·7	14·2	2·34	5·43	0·71	0·22	12·58	1·69
591·3	30	A	—	75·0	23·3	13·43	4·98	8·45	62·9	31·1	1·82	9·30	0·82	0·69	11·65	1·28
592·0	45	A	—	74·7	38·3	13·46	3·41	10·05	74·7	51·3	2·34	13·27	0·91	0·43	13·34	0·97
591·6	60	A	—	75·0	50·1	13·48	2·18	11·30	83·8	66·8	3·37	15·16	1·37	0·40	14·40	0·75
590·8	120	A	—	73·6	69·2	13·27	1·27	12·00	90·4	94·0	5·31	17·16	1·74	0·26	14·32	0·26
592·3	41 hr.	A	—	75·1	112·3	13·45	0·06	13·39	99·6	149·5	13·75	19·63	0·12	0	20·30	0·02
592·7	100 hr.	B	—	87·7	140·6	11·49	0·10	11·39	99·1	160·3	14·51	15·14	0·16	0	18·71	0·03

have been drawn. The result is remarkable since at the temperatures in question there should be no induction periods or, at most, only very short ones. The observed apparent induction periods are most probably due to the circumstance that in the initial part of the decomposition the gaseous reaction products have the same volume as the decomposed part of the reactant.

Making use of the linearity of $\log \frac{p_0}{p_t}$ with time in the early stages of decomposition, the rate constants at different temperatures have been calculated from the first figure of each series of measurements. The results in the case of disilane are evident from Table III, which for comparison also includes the rate constants found by Emeléus and Reid. Although this is not expressly stated, it must be assumed that their figures are given in min.$^{-1}$ units, and they have, therefore, here been converted to sec.$^{-1}$. As it will be seen the rate constants found by the present author are considerably higher than those of Emeléus and Reid, which result is easily understood from what has already been said.

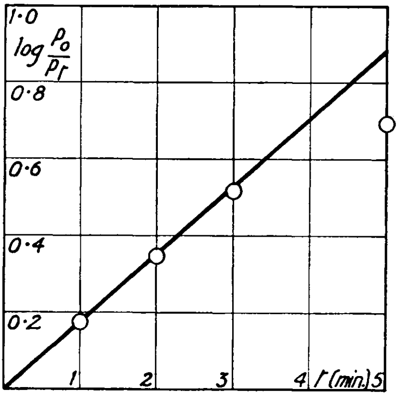

FIG. 3.

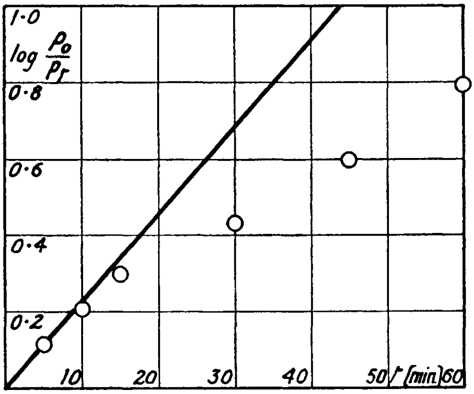

FIG. 4.

On the basis of the data of this table the following expression for the specific rate of decomposition as a function of the temperature has been obtained by the method of least squares : $k = 5{\cdot}8 \times 10^{14}\, e^{-\frac{48900}{RT}}$. The result has been plotted in Fig. 5.

TABLE III.—RATE CONSTANTS OF THE DECOMPOSITION OF Si_2H_6.

Temp. °K.	$\frac{1}{T} \times 10^3$.	k sec.$^{-1}$.	log k.	Experiments by E. & R.	
				Temp. °K.	k sec.$^{-1}$.
584·6	1·711	$2{\cdot}71 \times 10^{-4}$	$-3{\cdot}567$	587	$1{\cdot}0 \times 10^{-4}$
597·5	1·674	$7{\cdot}68 \times 10^{-4}$	$-3{\cdot}115$	605	$4{\cdot}2 \times 10^{-4}$
611·2	1·636	$2{\cdot}30 \times 10^{-3}$	$-2{\cdot}638$	622	$1{\cdot}1 \times 10^{-3}$
621·2	1·610	$3{\cdot}80 \times 10^{-3}$	$-2{\cdot}420$	633	$2{\cdot}8 \times 10^{-3}$
633·4	1·579	$6{\cdot}70 \times 10^{-3}$	$-2{\cdot}174$	—	—

The above equation indicates that the activation energy of decomposition of disilane should be 48·9 kcal., whilst Emeléus and Reid found 51·3 kcal. In spite of the differences in the rates of decomposition the agreement between the activation energies is good. It may be assumed, however, that this agreement is largely accidental.

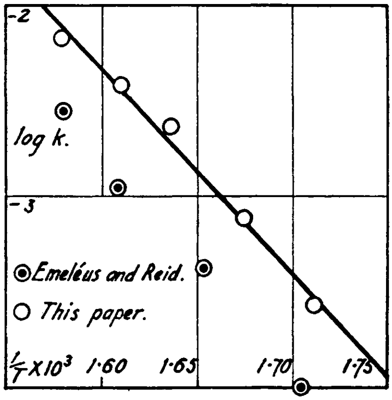

FIG. 5.

For the single series of experiments with trisilane the rate constant in the early stage of decomposition has been calculated to be 8·76 × 10^{-4} sec.$^{-1}$ at 591·5° K., whilst Emeléus and Reid obtained 2·57 × 10^{-4} sec.$^{-1}$ at 589° K. and 4·95 × 10^{-4} at 600° K. Thus, for trisilane also, the rate of decomposition has been found to be higher than that reported by the above-mentioned investigators.

Discussion.

Disilane.—Since the decomposition of the disilane follows a unimolecular course, the primary step must be a splitting of the molecule. The most probable alternatives then seem to be:

$$Si_2H_6 \rightarrow 2SiH_3 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$Si_2H_6 \rightarrow SiH_4 + SiH_2. \quad . \quad . \quad . \quad . \quad (2)$$

However, other initial reactions such as

$$Si_2H_6 \rightarrow Si_2H_5 + H$$

and

$$Si_2H_6 \rightarrow Si_2H_4 + H_2$$

are possible.

The two former reactions are entirely analogous to the initial steps proposed by Rice[7] and Rice and Herzfeld[8] and by Storch and Kassel[9] in the pyrolysis of ethane. A comparison between the decomposition mechanisms of disilane and ethane seems to be justified to a certain degree, while the reaction products show great analogies in the two cases. In the decomposition of ethane the products are chiefly ethylene and H_2 and small amounts of CH_4, C and higher hydrocarbons, whilst in the case of Si_2H_6 they are monosilane, H_2 and solid polymerised silicon hydrides and smaller amounts of higher silanes. As to the composition of the latter substance Table I shows that at the beginning of its formation the formula is near $(SiH_2)_n$, whilst in the later stages it is becoming, on the average, poorer in hydrogen. This result is in accordance with the investigations of Schwarz and Heinrich,[10] who found that polysilene decomposes at the temperatures in question.

It seems very reasonable to assume that the polysilene has been formed by polymerisation of silico-olefines. This assumption seems to be supported by the fact that in the initial stage of decomposition no polysilene is present. Since during this period there is no change of volume, there may at first be a conversion of disilane into monosilane and higher silanes. Because of the large concentration of disilane compared with the concentrations of radicals and silico-olefines, these latter substances may react with

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[7] Rice, *J. Amer. Chem. Soc.*, 1931, **53**, 1959.
[8] Rice and Herzfeld, *ibid.*, 1934, **56**, 284.
[9] Storch and Kassel, *ibid.*, 1937, **59**, 1240.
[10] Schwarz and Heinrich, *Z. anorg. Chem.*, 1935, **221**, 277.

disilane to form higher silanes rather than polymerise. The higher silanes, however, are less stable than disilane and decompose more rapidly, giving rise to new radicals and olefines. With decreasing amount of disilane collisions between unsaturated molecules become more frequent, leading finally to the formation of polysilene.

The decomposition of this latter substance is a heterogeneous process. Therefore, only the initial part of the decomposition of disilane can be treated as a purely homogeneous reaction. The study of the decomposition of ethane is a more easy one, since, with the exception of elementary carbon, only gaseous reaction products are formed. But although in this case a large amount of work in different directions has been done to discover the reaction mechanism, there still prevails considerable doubt about it. Even more difficult is the interpretation of the decomposition mechanism of disilane, since here the tendency of the unsaturated hydrides to polymerise eliminates characteristic features which would otherwise appear from the nature and amounts of the individual compounds. It seems, therefore, to be of little use to try to suggest a complete scheme for the decomposition mechanism, and in the present paper only a more limited discussion concerning the information to be derived from some experimental facts will be given.

It was suggested by Emeléus and Reid, by analogy with the then most widely accepted interpretation of the decomposition of ethane, that the decomposition of disilane is mainly a chain reaction of the Rice type, the initial step of which is the reaction (1). In support of this theory they stated that an increase of the surface-volume ratio decreased the rate of decomposition. However, since this result was probably obtained from determinations of pressure changes alone, further experiments with analysis of the reaction products ought to be performed before drawing a definite conclusion. Experiments with different surface-volume ratios at the same temperature have not been carried out by the present author, but Table I and Fig. 5 indicate that the influences of chain reactions would be small.

This result is in accordance with the view now commonly held in the case of ethane. Though it has been certainly found that chain reactions actually do take place in the decomposition of this substance, a large part of it proceeds by a chain-free mechanism. There exists at the present time very little knowledge about this part of the reaction. There appears, however, to be much to be said in favour of the mechanism suggested by Storch and Kassel. Their scheme involves the methylene instead of the methyl radical, and although there is still no certain experimental evidence as to the existence of methylene radicals in this case, the assumption of its participation explains the formation of the main reaction products in the simplest and most natural manner.

In addition to the decomposition experiments with pure disilane Emeléus and Reid also carried out investigations on the effects of added hydrogen and ethylene. The effect of hydrogen was to remove the induction period, and analyses of the reaction products showed that considerably more monosilane had been formed. This result they thought to give support to a mechanism of the Rice type. It will, however, at once be seen that both silyl and silene radicals may well account for the increased amount of monosilane.

The experiments quoted in the present paper show that at the temperatures in question there are most probably no induction periods at all. The induction periods found by the investigators mentioned above have been obtained from pressure readings and are only apparent. The disappearance of the induction periods when hydrogen is added is due to the change in the relative amounts of the different reaction products.

In the decomposition experiments on mixtures of disilane and ethylene there was a certain polymerisation of the latter compound. This result is quite analogous to that found when decomposing lead tetramethyl in the presence of ethylene as reported by Taylor and Jones.[11] However, whilst in the latter case each methyl radical produced caused on the average a polymerisation of 6-7 molecules of ethylene, the amount of this substance polymerised by the decomposition of disilane was only approximately equal to the amount of disilane decomposed. It may be that the polymerising effect of methyl radicals is greater than that of the silyl radicals. It seems, however, that the results in the two cases are too different to support the theory of a mechanism in which silyl radicals play the most important part.

A comparison of the rates of decomposition of the disilanes with light and heavy hydrogen shows that the deuterium disilane decomposes at a considerably lower rate than the ordinary compound. In a relatively narrow temperature range around 600° K. the average ratio of the decomposition rates, k_D/k_H, was 0·71. Although it was expected that the deuterium compound would be the more stable one, the difference seems to be too large if the rate-determining step in both cases is the split of the Si—Si bond. It is hardly reasonable to assume that the deuterium atoms attached to the silicon atoms should influence the strength of the Si—Si bond to such a high degree.

This difficulty does not arise if (2) is assumed to be the primary step. Here a rearrangement of the atoms within the molecules may be assumed to precede decomposition, and this process almost certainly requires a different activation energy in the two cases.

Considering the diamond arrangement of the atoms in the silicon crystal, the strength of the Si—Si bond should be simply one-half of the heat of sublimation of silicon. Unfortunately, the figures for this latter quantity obtained by different investigators from vapour pressure determinations show very large inconsistency, covering a range from 44 kcal. as previously found by von Wartenberg [12] up to 102-105·5 kcal. more recently obtained by Ruff.[13] It seems very reasonable to consider the latter figure as the most reliable one, and this would give a bond strength of 51-53 kcal., which is within the limits of error equal to the activation energy derived by Emeléus and Reid. (Pauling [14] gives 42·5 kcal. for the strength of the Si—Si bond.) In the opinion of the present author, however, the heat of sublimation of silicon is far too uncertain to give any valuable support to the assumed strength of the Si—Si bond. It seems on the contrary that the activation energy obtained for the decomposition of disilane should rather be used to choose the most reliable figure for the heat of sublimation, since the bond strength can hardly be assumed to be less than that of the activation energy.

However, owing to the complex nature of the decomposition, it seems doubtful whether the overall activation energy can be used as a measure of the rate of the initial reaction. The participation of the original disilane molecules in reactions with radicals and other molecules formed and the re-formation of disilane molecules in different ways make the whole problem very obscure. The activation energy seems to be rather high as it is only slightly smaller than that of the decomposition of the monosilane, viz., 51·7 kcal., found by Hogness, Wilson and Johnson [5] and confirmed by the present author. Finally, it may be mentioned that the decomposition of the analogous substance digermane, examined by Emeléus and Jellinek,[15] most probably is also more complex than reported by these investigators.

Trisilane.—In the decomposition of trisilane, the mechanism certainly

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[11] Taylor and Jones, *J. Amer. Chem. Soc.*, 1931, **52,** 1111.

[12] von Wartenberg, *Z. anorg. Chem.*, 1913, **79,** 71.

[13] Ruff, *Trans. Electrochem. Soc.*, 1935, **68,** 87.

[14] Pauling, *The Nature of the Chemical Bond* (New York, 1944).

[15] Emeléus and Jellineke, *Trans. Faraday Soc.*, 1944, **40,** 93.

is even more complex, more modes of decomposition being possible here. Emeléus and Reid suggested that the first step might be

$$Si_3H_8 \rightarrow 2SiH_3 + SiH_2.$$

However, such a simultaneous split of two Si—Si bonds must be rare, as it would most probably imply the accumulation within the molecule of a larger amount of energy than is required for the break of only one bond.

Decomposition experiments with trisilane mixed with an excess of hydrogen, carried out by the authors just mentioned, gave the result that almost exactly two moles of monosilane were formed per mole of trisilane decomposed. They explained this fact by assuming that the silyl radicals were hydrogenated to monosilane, whilst the silene radicals were dehydrogenated. However, if this assumption is correct, it would be expected that the decomposition of disilane in presence of an excess of hydrogen would also give two moles of monosilane per mole of disilane decomposed, since a simple splitting of a disilane molecule also gives two silyl radicals. But the experimental results [1] show that the maximum amount of monosilane obtained in this case is only 1·5 moles per mole of disilane.

Experiments with added ethylene gave an amount of polymerisation of ethylene of 1·33 moles per mole of trisilane decomposed. This result presumably indicates a somewhat larger concentration of silyl radicals than in the case of disilane.

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Summary.

The thermal decomposition of disilane in the temperature range 584-633° K. and of trisilane at 592° K. has been studied by a static method and with analyses of the reaction mixture. It has been found that there is no exact proportionality between the amount of silane decomposed and the observed change of pressure.

For both substances the rates of reaction at given temperatures have been found to be larger than those previously obtained. The induction periods reported by other investigators from observations of pressure changes have been shown to be only apparent.

The activation energy of the decomposition of disilane has been found to be 48·9 kcal., which is not much below the figure given previously, viz. 51·3 kcal.

Some arguments have been advanced that chain reactions involving silyl radicals may not be the most important process in the decomposition of the two compounds.

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