153. *The Oxidation of the Silicon Hydrides. Part II.*

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WE have already shown (J., 1935, 1182) that the oxidation of monosilane is a typical chain reaction, exhibiting the phenomena of a lower and an upper critical explosion limit, and a quantitative study was made of the effects of mixture composition, dimensions of the reaction vessel, and diluent gases on the lower limit, and of mixture composition, temperature, diluent gases, and inhibiting substances on the upper limit. The experiments described below include the examination of the effect of temperature on the lower limit for the oxidation of monosilane, and also of the ignition phenomena exhibited by disilane and trisilane, both of which were found to resemble monosilane. Lower and upper explosion limits were observed and have been studied in some detail. Finally, an attempt has been made to correlate the data obtained for the three hydrides, Semenoff's generalised theory of chain rections being used as a basis.

EXPERIMENTAL.

Disilane and trisilane were isolated in a state of purity by the method of Stock and Somieski (*Ber.*, 1916, **49**, 111), the vapour pressures agreeing closely with the standard values. The apparatus employed previously in studying the lower critical explosion limit phenomena was modified so as to allow the silicon hydride and oxygen to enter the evacuated reaction vessel simultaneously through calibrated capillaries (Fig. 1). This ensures that the two gases mix thoroughly, and has the added advantage that it eliminates the use of the method of trial and error in determining the lower limit. The reaction vessel *A* was connected to the vacuum line by the standard ground joint *G* and the tap 7. The fine capillaries c_1 and c_2, the flow through which was determined for various pressures of the two gases by measurements with a McLeod gauge, were used to admit the silicon hydride and oxygen into *A*. The main reservoirs of these gases were connected to smaller auxiliary reservoirs, and the pressure in the latter was adjusted and measured, before each experiment. In measuring the lower limit, the apparatus was evacuated with taps 1, 2, 3, 4, 7, 8, and 9 open. Taps 1, 4, and 7 were then closed, and 5 and 6 opened. Simultaneously the stop-watch was started. After an interval of several minutes a glow appeared suddenly throughout *A*, but not in the quill connecting tubes. The pressures of the two reactants at the moment of ignition were calculated from the calibration data for the two capillaries.

The apparatus was then re-evacuated, and a fresh determination made, with different rates of flow of the two gases, after adjustment of the pressures in the auxiliary reservoirs.

The reaction vessel *A* was not coated with sulphuric acid as in the earlier experiments. Its inner surface was washed with a few c.c. of 50% hydrogen fluoride and rinsed with distilled water; it was surrounded by an electrically heated furnace of Pyrex glass and of 10 cm. internal diameter. The temperature was constant to within ± 2°. The volume of the dead space in the reaction system was not more than 4% of the volume of *A*.

The experimental method used in studying the upper critical explosion limit phenomena for disilane and trisilane was the same as that used for monosilane (*loc. cit.*).

Results.

Lower Critical Limits for Mono-, Di-, and Tri-silane.—The lower limit for monosilane was measured at 100°, the temperature previously used in studying its upper limit. The cylindrical reaction vessels had diameters 2·32, 3·04, and 4·86 cm., and were 20 cm. long. For disilane and trisilane the diameters were 1·30, 2·32, 3·04 cm. Measurements with the last substances were made at 0°. The surface of the reaction vessel was treated with hydrofluoric acid in each case, and was then allowed to become coated with a thin film of silica, which accumulated in successive experiments.

FIG. 1.

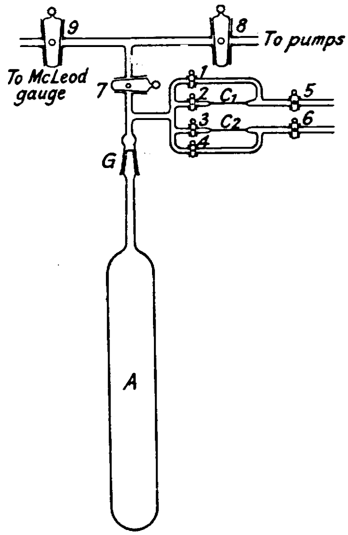
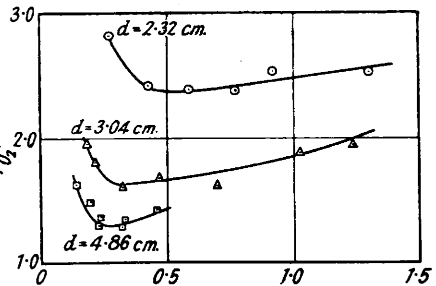


FIG. 2.



Effect of vessel diameter on lower limit for monosilane.

The curves shown in Figs. 2, 3, and 4 give the relation between the partial pressures of the silicon hydride and oxygen for reaction vessels of different diameters. The three sets of curves all show a lowering of the pressures as the diameter of the reaction vessel is increased. The critical pressures for silane–oxygen mixtures are of the order of 1·5—4 mm. For disilane–oxygen mixtures they are lower (0·1—1·0 mm.), and for oxidation of trisilane, which is generally regarded as spontaneously inflammable, the lower critical explosion limits lie at pressures of the order of 0·01—0·1 mm. In spite of the low magnitudes of these pressures, the experiments were strikingly reproducible. Over the pressure ranges shown in the diagrams the ignition was very sharply defined. Mixtures containing more than 50% of disilane gave a feeble glow, which became increasingly difficult to detect as the proportion of hydride was increased. The inflammation curves for trisilane are very steep, but the phenomena may be examined readily up to a point where the mixture contains 75% of hydride. The form of the curve for monosilane (Fig. 2) is somewhat unusual in that it shows a minimum, but this is adequately accounted for in the discussion of the reaction mechanism.

The general theory of chain reactions requires that the relationship $p_K^2 . d^2 . f(x) =$ const. should hold at the lower critical oxidation limit when studied in tubes of different diameter. In this equation, p_K is the lower critical pressure, d the diameter of the reaction vessel, and x the proportion of hydride in the gas mixture. If x is constant, and d is varied, the value of p_Kd should be constant. In Table I, values of the product p_Kd are given for each of the three hydrides.

The constancy of the product p_Kd for any given reaction mixture in tubes of various diameters is very satisfactory, particularly with disilane. When the value of p_K is plotted against x for a given value of d, the curve obtained shows a minimum at $x = 0·15$ for monosilane and at $x = 0·50$ for disilane. For trisilane no minimum was observed up to $x = 0·70$. The significance of this minimum in relation to the reaction mechanism is discussed on p. 682.

TABLE I.

SiH$_4$ (100°).				Si$_2$H$_6$ (0°).				Si$_3$H$_8$ (0°).			
x.	$p_K d$.			x.	$p_K d$.			x.	$p_K d$.		
	d = 2·32.	3·04.	4·86.		d = 1·30.	2·32.	3·04.		d = 1·30.	2·32.	3·04.
0·10	6·95	6·25	8·07	0·10	0·768	0·836	0·755	0·10	—	0·116	0·111
0·15	6·62	5·80	7·45	0·20	0·494	0·551	0·425	0·20	0·100	0·079	0·082
0·20	6·86	6·17	8·00	0·30	0·423	0·429	0·380	0·30	0·069	0·061	0·063
0·25	7·40	6·94	9·30	0·35	0·396	0·404	0·371	0·40	0·055	0·050	0·050
0·30	8·21	7·79	—	0·40	0·385	0·385	0·371	0·50	0·047	0·042	0·043
0·40	—	10·45	—	0·45	0·380	0·377	0·377	0·60	0·043	0·037	0·038
				0·50	0·388	0·366	0·377	0·70	0·039	—	—

The above values of p_K for monosilane are considerably higher than those obtained with tubes coated on the inside with concentrated sulphuric acid. This fact must be attributed to the different capacities of the two surfaces for breaking chains, the sulphuric acid surface being less efficient. Dissolution of either gas in the sulphuric acid, or contamination of the reactants by the acid, would tend to raise the lower limit. Glass surfaces which were washed only with distilled water gave higher values for p_K, but they were very erratic.

Effect of Temperature on the Lower Limits.—The lower critical explosion pressure of monosilane was found to increase with the temperature, an anomaly traced to a slow reaction taking place below the limiting pressure; this reaction was imperceptible at 100°. For instance, when the addition of monosilane and oxygen through the capillary leaks was interrupted for periods of ½—1½ hours, ignition took place at the same pressure (within 5%) as when the gases flowed into the reaction vessel without interruption. At 145° and 200° a similar interuption in the addition of gas increased the apparent critical pressure. Results of such experiments are shown in Table II. The proportion of silane in the gas mixture is given in col. 2; col. 3 gives the fraction of the total gas added before the experiment was interrupted, col. 4 the period for which the experiments was interrupted, and col. 7 the percentage increase in the values of p_K.

TABLE II.

Temp.	SiH$_4$, %.	Fraction before interval.	Time interval (mins.).	p_K (obs.) (mm.).	p_K (continuous flow) (mm.).	Increase, %.
100° d = 4·86 cm.	12·3	0·83	45	1·52	1·57	—
	15·6	0·64	120	1·55	1·53	—
145° d = 3·04 cm.	18·1	0·38	10	3·57	3·06	14
	17·2	0·60	10	3·67	3·04	17
	10·7	0·41	10	3·69	3·12	15
193° d = 3·04 cm.	19·3	0·30	6	4·88	3·45	41
	20·3	0·36	6	5·36	3·60	49
	19·7	0·68	6	4·53	3·50	29
	17·4	0·42	60	4·20	3·20	31
	13·9	0·64	45	4·60	3·20	44

The effect of temperature on the lower limit for disilane is apparently normal. Results obtained at 0°, 100°, and 193° are shown in Table III (data from smoothed curves). The limiting pressure falls with increase in temperature. This does not mean that there was no slow reaction below the lower limit, but rather that it was insufficient at the very low pressures used to produce the anomalous results found with monosilane. This would indicate that any reaction below the lower critical explosion limit is a surface reaction. Tests were made in the case of the measurements at 0° to determine the effect of interrupting the addition of the reacting gases, but the change in the lower limit was inappreciable for times of interruption up to 1 hour.

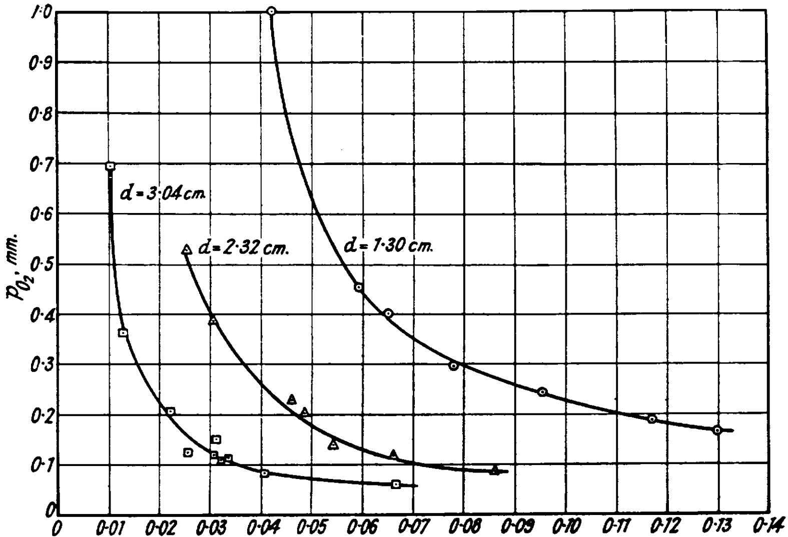
TABLE III.

Effect of temperature on p_K *for* Si$_2$H$_6$ (d = 3·04 cm.).

SiH$_4$, %.	10	20	30	40	50
	p_K (mm.).				
Temp.					
0°	0·220	0·147	0·126	0·122	—
100	0·160	0·101	0·079	0·067	0·062
193	0·134	0·084	0·063	0·050	0·045

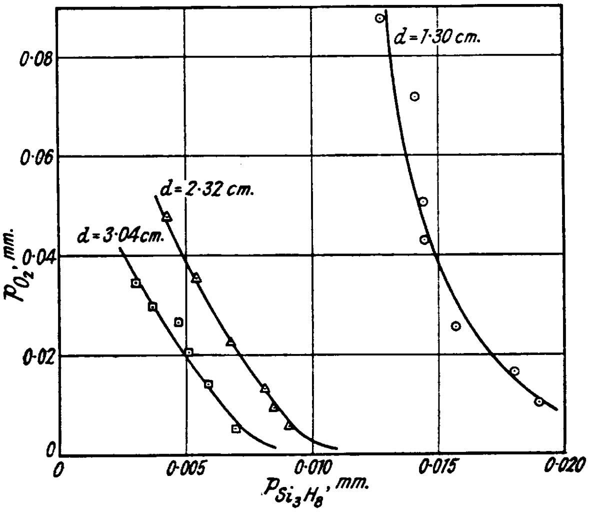
Upper Critical Explosion Limits of Disilane and Trisilane.—The upper limit phenomena for these two hydrides were studied at 0°. It was found possible to use the same method as for monosilane (Emeléus and Stewart, *loc. cit.*). Either hydride could be mixed with oxygen at total pressures of 40—70 cm., provided that the percentage of hydride in the mixture was low. Great care was needed, however, in mixing the gases, and it was necessary to evaporate the silicon hydride very slowly into the oxygen atmosphere after the two gases had been introduced into the reaction vessel. If bumping of the liquid hydride occurred, the mixture exploded, owing to local enrichment of the gas mixture in hydride. This risk was particularly great with trisilane, and only a limited number of experiments on its upper critical explosion limit were successful.

FIG. 3.



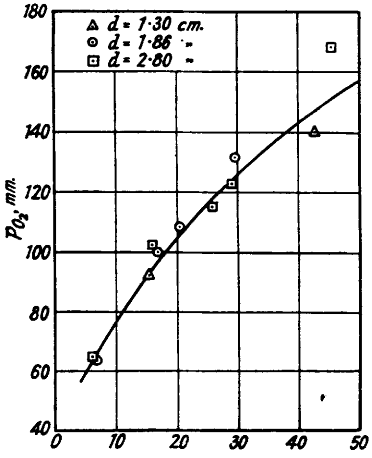
Effect of vessel diameter on lower limit for disilane.

FIG. 4.



Effect of vessel diameter on lower limit for trisilane.

FIG. 5.



The upper limit phenomena for disilane resemble those for monosilane; the diameter of the reaction vessel had no appreciable effect on the limit. The results are shown in Fig. 5, in which readings with reaction tubes of diameter 1·30, 1·86, and 2·80 cm. are included. The experiments were carried out at 0°. The relation between the pressures of the reactants in the limit mixture is

$$[\mathrm{O_2}] + 0{\cdot}81[\mathrm{Si_2H_6}] = 625[\mathrm{Si_2H_6}]/[\mathrm{O_2}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(a)}$$

This equation is used in the discussion in deducing certain constants for the reaction. The value of the upper critical pressure increases steadily with increasing concentrations of disilane. This was also an outstanding characteristic of the oxidation of monosilane at 100° (Emeléus and Stewart, *loc. cit.*).

Increase in temperature raised the value of the critical pressure, as shown by the data in Table IV, obtained with mixtures containing 10% of disilane. The values p_K (calc.) are those calculated from the general equation for inflammation based on the theory of chain reactions (p. 683).

TABLE IV.

Temp.	0°	16·5°	30·0°	36·0°	44·5°
p_K (obs.)	70·5	119	145	153	186
p_K (calc.)	70·5	105	139	156	182

The magnitudes of these critical pressures for disilane at 0° are of the same order as those of monosilane at 100°. To some extent this is a manifestation of the increase in " inflammability " of the silicon hydrides as the homologous series is ascended.

The effect of small concentrations of ethylene on the upper limit for disilane at 0° was studied with a constant ratio (0·25) of disilane to oxygen. The results are tabulated below, and it will be seen that the ethylene acts as an inhibitor of the explosion, its effect being very similar to that on the oxidation of monosilane: no doubt a great number of typical inhibitors of oxidation reactions would act similarly.

p_K (mm.)	167	133	107	100	77	65
$p_{\mathrm{C_2H_4}}/p_{\mathrm{O_2}} \times 10^2$	0	0·17	0·31	0·63	1·15	2·0

The few observations made on the upper limit of trisilane at 0° are given below. The proportion of hydride must be very low for it to be possible to obtain a mixture with oxygen. Nevertheless, such a mixture can be obtained, and explodes when the total pressure is reduced. The values tabulated under p_K (calc.) were calculated from the equation given on p. 683.

A more extensive study of the critical oxidation phenomena of trisilane would be possible if the experiments could be conducted at a lower temperature. A limit would, however, be set by the vapour pressures of the liquid hydride.

TABLE V.

$\mathrm{Si_3H_8/O_2}$	0·0145	0·0124	0·0107
p_K (calc.), mm.	281	240	207
p_K (obs.), mm.	252	223	255

DISCUSSION.

The following mechanism for the oxidation of monosilane was suggested by the authors (*loc. cit.*):

$$\mathrm{SiH_4} + \mathrm{O} = \mathrm{SiH_2} + \mathrm{H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{SiH_2} + \mathrm{O_2} = \mathrm{SiH_2O} + \mathrm{O} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{SiH_2O} \longrightarrow \overset{\mathrm{O_2}}{\ldots\ldots} \longrightarrow \mathrm{SiO_2} \;. \quad \text{(degenerate branching)}$$

$$\mathrm{O^*} + \mathrm{O_2} = \mathrm{O} + \mathrm{O_2^*} \; . \; . \; . \; . \quad \text{(energy branching)}$$

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} = \mathrm{O_3} + \mathrm{M} \quad . \quad \text{(gas-phase deactivation)}$$

$$\mathrm{O} \text{ or } \mathrm{SiH_2} + \text{wall} \; . \; . \; . \; . \quad \text{(surface deactivation)}$$

If q_1 and q_2 collisions are necessary for reactions (1) and (2) respectively to take place, the general equation defining the upper and lower critical explosion pressures as the proportions of the reactants are changed is

$$1 + \varepsilon\frac{q_1}{\delta}\frac{[\mathrm{O_2}]}{[\mathrm{SiH_4}]} = \left(\frac{z_3}{z_2}\mu\right)\cdot\frac{q_1}{\delta}\frac{[\mathrm{O_2}]}{[\mathrm{SiH_4}]}\{[\mathrm{O_2}] + [\mathrm{SiH_4}]\} + 3{\cdot}65\frac{\lambda_0^{\,2}}{d^2}\,\frac{\frac{q_1}{\delta}[\mathrm{O_2}] + \frac{q_2}{\delta}[\mathrm{SiH_4}]}{[\mathrm{O_2}][\mathrm{SiH_4}]\{[\mathrm{O_2}] + [\mathrm{SiH_4}]\}} \;. \qquad (3)$$

where pz_3/z_2 is the ratio of triple to double collisions at the pressure p, which equals to the sum of $[O_2] + [SiH_4]$; ε, δ, and μ are respectively the probabilities of reaction in a collision between atomic and molecular oxygen, of branching at any given link, and of gas-phase deactivation, λ_0 is the mean free path at 1 mm. pressure and d is the diameter of the reaction vessel. If this equation is first applied to the lower-limit data, deactivation by triple collisions (represented by the first term on the right-hand side) may be neglected. The value $\varepsilon q_1/\delta = 0{\cdot}202$, previously found from the limit for silane at 100°, may be inserted.

Further, we may put $[O_2] = (1 - x)p_K$ and $[SiH_4] = xp_K$, where x is the proportion of monosilane in the reaction mixture, and p_K is the lower critical oxidation limit at 100°. Equation (3) then reduces to

$$p_K{}^2\left\{1 + 0{\cdot}202\left(\frac{1-x}{x}\right)\right\} = \frac{3{\cdot}65\lambda_0{}^2}{d^2}\left\{\frac{q_1}{\delta}\cdot\frac{1}{x} + \frac{q_2}{\delta}\cdot\frac{1}{1-x}\right\} \quad . \quad . \quad . \quad (4)$$

When the experimental values of p_K for silane (Table I) are plotted against x a minimum is found at $x = 0{\cdot}15$. This minimum value can be applied to obtain a value of the ratio q_2/q_1 by differentiating equation (4) and inserting in the resulting expression the value $x = 0{\cdot}15$. It is thus found that $q_2/q_1 = 2{\cdot}61$, *i.e.*, 2·61 times as many collisions between a SiH_2 radical and molecular oxygen are needed for reaction as in the reaction of atomic oxygen and monosilane. The values of q_1/δ and q_2/δ derived therefrom are $1{\cdot}52 \times 10^5$ and $3{\cdot}96 \times 10^5$; also, $(z_3/z_2)\mu = 1{\cdot}51 \times 10^{-8}$ and $\varepsilon = 1{\cdot}33 \times 10^{-6}$.

The values of q_1 and q_2 are inseparable from δ, the probability of branching. It is considered probable, however, that δ will vary exponentially with temperature, in which case q/δ can be written in the form $e^{E/RT}$.

This form is used in discussing the results for disilane below, where the effect of temperature on the upper critical oxidation limit has to be considered.

Oxidation of Disilane.—The kinetics of the oxidation of disilane may be represented by a reaction scheme similar to that for monosilane. The active centre which initiates the reaction is assumed to be atomic oxygen. Thus :

$$Si_2H_6 + O = Si_2H_4 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$Si_2H_4 + O_2 = Si_2H_4O + O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$Si_2H_4O \longrightarrow \overset{O_2}{\ldots\ldots} \longrightarrow SiO_2 \quad . \quad . \quad \text{(degenerate branching)}$$

$$O + O_2 + M \longrightarrow O_3 + M \quad . \quad . \quad . \quad \text{(gas-phase deactivation)}$$

$$O \text{ or } Si_2H_4 + \text{wall} \longrightarrow \text{surface deactivation.}$$

If q_1 and q_2 have the same meaning as before with reference to equations (5) and (6) respectively, and if $q_1/\delta = e^{E_1/RT}$ and $q_2/\delta = e^{E_2/RT}$, the complete equation for inflammation is

$$\left(\frac{z_3}{z_2}\right) e^{E_1/RT}\frac{[O_2]}{[Si_2H_6]}\{\mu_1[O_2] + \mu_2[Si_2H_6]\} + 3{\cdot}65\frac{\lambda_0{}^2}{d^2}\frac{e^{E_1/RT}[O_2] + e^{E_2/RT}[Si_2H_6]}{[O_2][Si_2H_6]\{[O_2] + [Si_2H_6]\}} = 1 \ . \quad (7)$$

At the lower limit, deactivation by triple collisions, represented by the first term in equation (7), is neglected. It is then found, by the method used for monosilane, that $q_1 = q_2$. This is inherent in the data in Table I, where the minimum in the relationship between p_K and x is shown to occur at approximately $x = 0{\cdot}5$. It is also found that $q_1\delta = q_2/\delta = 900 = e^{3700/RT}$ (for $T = 273°$).

The effect of temperature on the lower-limit phenomena is represented by the equation

$$\log_{10} p_K/T = \bar{E}/2{\cdot}3RT + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This equation was developed by Semenoff and allows for the loss of heat from the gas. It replaces the equation $\log p = \bar{E}/RT + B'$, and the constant $\bar{E} = E/2$. Insertion of experimental values of the lower limit of disilane into equation (8) gives a value of $\bar{E} = 1830$ g.-cals., *i.e.*, $E = 3660$ g.-cals. This value of E is in good agreement with the value, 3700, calculated from equation (7).

At the upper limit, wall deactivation is neglected and equation (7) reduces to the same form as the experimental equation [(a), p. 681]. By comparing the constants of these two equations, and inserting the value $q/\delta = 900$ deduced from the lower-limit data, it is found that $\mu z_3/z = 1{\cdot}78 \times 10^{-6}$ and $\mu_2/\mu_1 = 0{\cdot}81$.

In equation (7) the term $e^{E/RT}$ ($= q/\delta$) governs the influence of temperature, and it is possible to use the value $q/\delta = 900$, deduced from the lower limit, to predict the temperature variation of the upper limit of disilane. Values calculated in this way are included in Table IV and agree well with the experiment.

The lower-limit results for trisilane show no minimum in the plot of p_K against x for values of x up to 0·75, though a minimum must occur for still higher values. The mechanism of the oxidation of trisilane is probably similar to those for mono- and di-silane, two active centres being required for chain propagation, one of which is the oxygen atom. If, as before, q_1 and q_2 collisions are needed for these two reactions to take place, q_1 and q_2 may be taken as equal to a first approximation. It can then be shown on the experimental data on the lower limit for trisilane that $q/\delta = 30$, corresponding with a very low energy of activation. This approximation enables us to predict the values of the upper limit of trisilane. If the value $\mu z_3/z_2 = 1{\cdot}78 \times 10^{-6}$ found for the oxidation of disilane is inserted, the equation for the *upper* critical limit, derived in the same manner as for disilane, is $p_K = 1{\cdot}94 \times 10^4[Si_3H_8]/[O_2]$. Values of p_K calculated from this relationship are shown in Table V, and it is seen that the agreement is better than would be expected from the assumptions made.

The results of Schantarowitsch on the oxidation of monosilane (*Acta Physicochim. U.R.S.S.*, 1935, **2**, 633) lead to the same general conclusions as the experiments described in this paper. There is, however, one outstanding discrepancy. Our monosilane was decidedly more readily inflammable than that used by Schantarowitsch: it gave lower values for the lower limit, and lower values for the minimum ignition temperature of a given mixture. The vapour-pressure measurements of our material agreed with the values published by Stock and Somieski (*loc. cit.*). Reaction with alkali gave exactly the theoretical amount of hydrogen. Finally, the absorption spectrum, which was examined in connection with work in progress on the photodecomposition and oxidation of these hydrides, also afforded no evidence of appreciable contamination by higher hydrides. Schantarowitsch prepared monosilane from silicochloroform, and showed that the product after fractionation gave the theoretical volume of hydrogen when treated with alkali. In these circumstances the discrepancy between the two sets of results must be due either to a trace of more inflammable hydride in our material, to a trace of inhibiting substance in Schantarowitsch's, or to differences in the surface conditions in the two sets of experiments.

The lower critical oxidation for monosilane has been studied recently by Gutschmidt and Clusius (*Z. physikal. Chem.*, 1935, *B*, **30**, 265), who compressed the gas mixtures by allowing mercury to flow into the reaction vessel. In our experience this method does not readily yield reproducible results: a luminescence is sometimes observed at the surface of the moving mercury meniscus before the limiting pressure is reached.

Norrish's mechanism (*Proc. Roy. Soc.*, 1935, *A*, **150**, 36) for the oxidation of methane is essentially of the same type as that developed independently by the authors to account for the chain oxidation of monosilane. It was shown by Schantarowitsch (*loc. cit.*) that the explosive oxidation of monosilane occurs at a lower temperature if a trace of nitrogen dioxide is added. This experiment finds its counterpart in the sensitisation of methane explosion by nitrogen dioxide. The main points of difference between oxidation of hydrocarbons and of silicon hydrides are (i) that the latter ignite at much lower temperatures, and (ii) that the transition from the slow oxidation to explosion is far more rapid in the case of the silicon hydrides. The work is being extended with the object of elucidating these points of difference.

SUMMARY.

(1) The lower critical explosion pressures of mono-, di-, and tri-silane in dry glass reaction vessels have been studied.

(2) The upper critical explosion pressures of the last two have been studied.

(3) The effect of increase of temperature on these limits is to diminish the lower pressure limit and to raise the upper limit.

(4) The three hydrides form a graded series, in which the inflammability increases with the molecular weight.

(5) The results have been analysed on the theory of chain reactions, and certain conclusions deduced.

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