281. *The Oxidation of the Silicon Hydrides. Part I.*

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THE silicon hydrides form a group of compounds of graded thermal stability and chemical reactivity. The first member of the series, silane, can be mixed with oxygen under certain conditions without inflammation, whereas silicoethane and higher hydrides are spontaneously inflammable. The investigation of the interaction of these hydrides with oxygen was undertaken with the object, first, of determining if the oxidation occurs as a chain reaction, and, secondly, of furnishing data for comparison with the well-known oxidation phenomena of carbon compounds. Previous work in the field is very scanty. Friedel and Ladenburg (*Annalen*, 1867, **143**, 124) reported that mixtures of silane and oxygen ignited spontaneously when the pressure of the gas mixture was reduced. Stock and Somieski (*Ber.*, 1922, **55**, 3961) attempted to moderate the reaction by cooling the reactants to − 110°, but at this temperature the gases could be mixed (at low pressures) without violent explosion only if excess of nitrogen was present. The violence of the explosions was attributed by Stock to detonation of a hydrogen–oxygen mixture formed at an intermediate stage in the oxidation. Work on the oxidation of silicon hydrides by Schantarowitsch, of which only the general conclusions are available (Semenoff " Chemical Kinetics and Chain Reactions," 1933, 376), appears to harmonise with the results described below.

EXPERIMENTAL.

Preparation of Materials.—Pure silane was prepared, according to Stock and Somieski (*Ber.*, 1916, **49**, 111), by dropping magnesium silicide into 20% hydrochloric acid, washing the evolved gas with water, drying it with calcium chloride and phosphoric anhydride, and condensing it in liquid nitrogen. The mixture of silicon hydrides so obtained was separated by fractional condensation in a vacuum apparatus of the type described by Stock and Somieski (*loc. cit.*, 1916). Mercury valves were used throughout in place of taps. Hydrides other than silane were completely removed by slow distillation in a vacuum through a U-tube cooled to − 125°. The monosilane passed through this bath (higher hydrides being condensed), and was stored in a globe with a mercury valve. Vapour-pressure measurements on the material used gave the following values (those of Stock and Somieski are in parentheses) : −126·6°, 28·79 cm. (28·85) ; − 123·3°, 38·69 cm. (38·60) ; − 119·0°, 49·80 cm. (50·02). Temperatures were measured with an ethylene vapour-pressure thermometer.

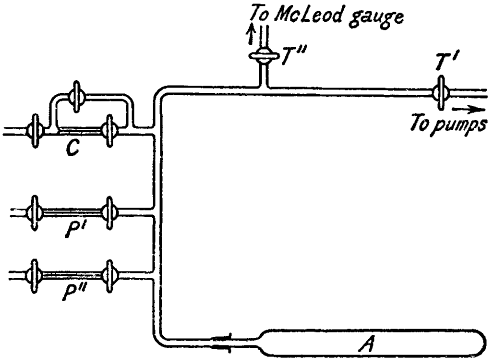
Oxygen, prepared by heating potassium permanganate in a vacuum, was purified by passage through a trap cooled in liquid air, and collected in a globe. The nitrogen used was taken from a commercial cylinder, and purified by passage over red-hot copper gauze. Both sulphur dioxide and ethylene were purified before use by fractional distillation in a vacuum.

Nature of the Reaction.—In a series of preliminary observations it was found that, on allowing oxygen to leak through a fine capillary into a tube containing silane at a pressure of about 1 mm., there was no evidence of reaction until a certain amount of oxygen had accumulated. At this limiting oxygen pressure a faint flash (visible only in the dark) passed through the gas mixture, and a white deposit formed on the walls of the reaction tube. A similar flash was observed on compressing a silane–oxygen mixture, initially at a very low pressure, in a McLeod gauge.

Silane-oxygen mixtures at 1 atm. pressure containing more than about 50% of silane could not be prepared at room temperature without explosion taking place. Explosions were mild with less than 40% of silane. For mixtures with 40—60% of silane, the explosion was violent and generally shattered the apparatus. With still richer mixtures it was milder, but took place even at 0—20°. In the explosion of such mixtures, a brown deposit was formed, which, according to Stock and Somieski (*loc. cit.*, 1922), consists of partially oxidised material (*e.g.*, $SiH_{1\cdot 9}O_{1\cdot 3}$). Reaction mixtures with less than about 30% of silane did not ignite at room temperature and atmospheric pressure, but, when heated to 100°, the pressure being reduced slowly by connection to a pump, explosion took place at a sharply defined limiting pressure. These lower and upper critical explosion limits are well-known characteristics of branching chain reactions, and have already been observed in the oxidation of phosphorus vapour, phosphine, sulphur, and other substances.

In the investigation described below, the effect of various factors on these explosion limits in the oxidation of silane has been studied. At the lower limit, the relation between the limiting pressures of silane and oxygen necessary for ignition to take place, and the effect of the diameter of the reaction vessel and of the addition of nitrogen on the limits were examined. At the upper limit, the effects of temperature, mixture composition, diluent gases (nitrogen and helium), and inhibiting substances (ethylene and sulphur dioxide) have been studied. No analyses of the explosion products of silane-rich mixtures were carried out. For upper-limit mixtures with 15—30% of silane the reaction was $SiH_4 + 2O_2 = SiO_2 + 2H_2O$, as deduced from the decrease in pressure in the explosion : after the resulting steam had been allowed to condense, and on the assumption that the gases were saturated with water vapour, the decrease in pressure was three times the pressure of silane taken. Furthermore, the white solid reaction product was incapable of reacting with further oxygen. For instance, after explosion of a mixture containing 20% of silane by reduction of pressure at 100°, the apparatus was rapidly evacuated, and a further 10·2 cm. pressure of oxygen was admitted. After 15 mins.' heating at 100°, the residual pressure was 10·3 cm. A number of tests were also made to determine if the residual gas after explosion of these oxygen-rich mixtures was completely absorbed by sodium hydrosulphite. This was invariably the case, showing that no free hydrogen was formed in the explosion.

Fig. 1.

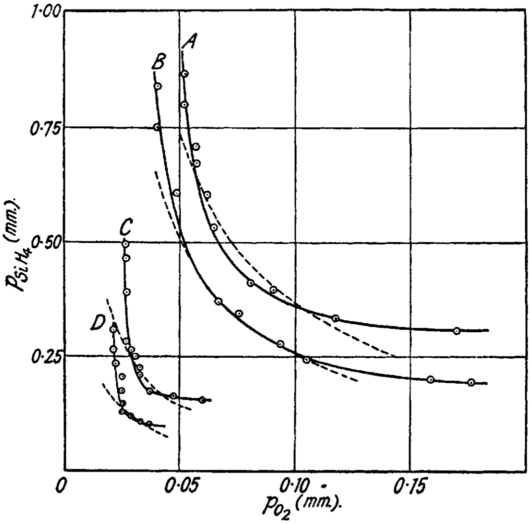


The Lower Critical Oxidation Limit.—The apparatus used in studying the lower limit is shown in Fig. 1. The reaction vessel *A* was a horizontal cylindrical tube 30—40 cm. long. It was connected by a standard taper, which permitted tubes of various diameters to be substituted readily. Oxygen was admitted through a capillary leak *C*. A series of calibration experiments was carried out with the McLeod gauge, in order to determine the pressure established in the reaction system with varying times of admission of oxygen. Silane and nitrogen were supplied from reservoirs containing these gases at known pressures, by the calibrated capillary pipettes *P'*, *P''*. All connections were of narrow quill tubing.

The observations on the lower limit were all made at room temperature (15° ± 2°) with the inside of the reaction vessel *A* moistened with a fresh film of concentrated sulphuric acid, which was renewed between experiments by turning *A* slowly. In dry glass tubes, or in contact with mercury, the results were not reproducible. The apparatus was first evacuated to a measured pressure of 10^{-4} mm., the taps *T'*, *T''* being then closed. Oxygen was then allowed to leak in for a measured time, and a known amount of silane (corresponding with a known pressure in the reaction system) was admitted from *P'*. The quantity of silane was readily controlled by adjusting the pressure at which *P'* was filled. The silane was admitted in the dark, and if a flash was observed, the experiment was repeated with less oxygen and the same amount of silane until a limiting pressure was reached at which the mixture just flashed. A series of such limiting pressures was then obtained for varying silane pressures. This experimental arrangement has the obvious disadvantage that mixing of the gases may be incomplete. This error was, however, lessened by the facts that the silane pressure in a limit mixture was always considerably in excess of the oxygen pressure, and that there was a lag in ignition (which increased with the oxygen pressure). The flash always took place throughout the tube *A*.

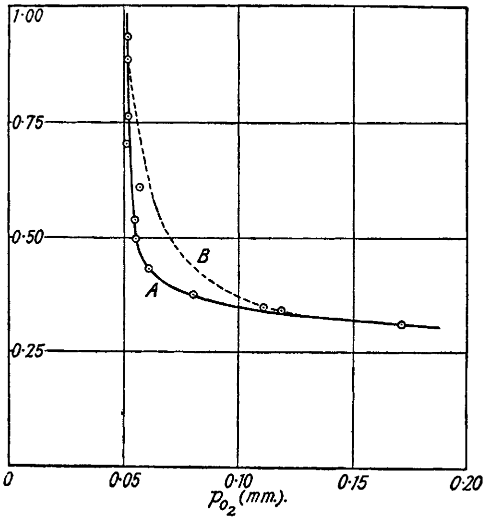
Results obtained for silane–oxygen mixtures in four tubes of diameters varying from 1·03 to 2·67 cm. are shown in Fig. 2, where the partial pressures of the reactants at the limits are plotted. The experimental values shown are the mean for mixtures which just ignited and just failed to ignite. The limit could be found with an estimated accuracy of ± 5% of the oxygen pressure. Owing to the faintness of the flash and to the lag in its appearance, it was essential to make the observations in a dark room.

FIG. 2.



Influence of tube diameter : A, 1·03 *cm. B,* 1·24 *cm. C,* 1·86 *cm. D,* 2·67 *cm.*

FIG. 3.



Influence of nitrogen on the lower limit. A, constant pressure of nitrogen = 0·110 *mm. B, nitrogen absent.*

The central portions of the above curves approximate to rectangular hyperbolæ (shown by broken lines in the diagram). In the Semenoff theory of chain reactions, the expression $d^2 . p_{O_2} . p_{SiH_4}$ at the lower limit should be constant, *d* being the diameter of the tube *A*. This is shown in the table below to be approximately true. The experimental values used in calculating this product are taken from the central portion of the curve (Fig. 2). The divergence from the hyperbolic relationship is much more marked in the two lowest curves (*d* = 1·86 and 2·67 cm.). There is apparently some factor operative here which is not taken into account by the simple theory, and which further experiments may elucidate.

d (cm.)	1·03	1·24	1·86	2·67
$d^2 . p_{O_2} . p_{SiH_4}$	0·0387	0·0389	0·0247	0·0238

In Fig. 2 the region of inflammation lies to the right of the four curves. Below a certain oxygen pressure, ignition did not occur with the highest pressure of the silane used, and *vice versa*. The asymptotic limiting pressures of silane and oxygen were inversely proportional to the tube diameter. Hinshelwood and Dalton's results on the lower limit of phosphine (*Proc. Roy. Soc.*, 1929, **125**, *A*, 294) show a similar divergence from the hyperbolic relationship when one of the reactants is in excess. The phosphine and oxygen pressures in their experiments were of the same order of magnitude, whereas in our experiments, the silane pressure was always much larger than that of the oxygen. This agrees with observations made on the upper limit, which show that at room temperature only silane-rich mixtures will ignite.

Influence of Nitrogen on the Lower Limit.—The influence of nitrogen was studied in a reaction tube of 1·03 cm. diameter. A series of experiments was made, as already described, to determine the limiting oxygen pressure for each of a number of silane pressures, but in every experiment a definite and constant amount of nitrogen was added to the oxygen from the pipette *P''* before admission of silane. In Fig. 3 results so obtained are recorded. The upper curve is the normal relation between the two gas pressures in absence of nitrogen; the lower curve shows the effect of a constant nitrogen pressure of 0·110 mm. The curves illustrate the depression of the lower critical limit in the presence of a diluent gas, indicating that the oxidation of a silane is a branching chain reaction. The Semenoff theory of such reactions requires that the expression

$$d^2 \cdot p_{O_2} \cdot p_{SiH_4} \, [1 + p_{N_2}/(p_{O_2} + p_{SiH_4})]$$

should be constant, if the function of the diluent gas is to prevent breaking of chains on the vessel walls. In Table I are data which show in the last col. the approximate constancy of this expression: the values of p_{O_2} and p_{SiH_4} used are those in the central portion of the smoothed curve. All pressures are in mm.

TABLE I.

p_{SiH_4}.	p_{O_2}.	p_{N_2}.	$p_{O_2} \cdot p_{SiH_4}$.	Value of expression.
0·500	0·055	0·110	0·0275	0·033
0·450	0·058	0·110	0·0261	0·032
0·400	0·066	0·110	0·0264	0·033

There was a definite lag in the ignition of silane–oxygen mixtures at the lower limit, as illustrated by the following values :

p_{SiH_4} (mm.) ...	0·233	0·171	0·0998	0·262	0·206	0·172
p_{O_2} (mm.)	0·022	0·0246	0·0361	0·0285	0·032	0·036
lag (secs.)	60	120	300	20	90	110

The first three observations were in a tube of 2·5 cm. diameter, and the last three in one of 2 cm. diameter. It is unlikely that this lag is due to diffusion, because of the relatively long times observed, and we are unable to explain it, but further data are being accumulated under more varied conditions.

FIG. 4.

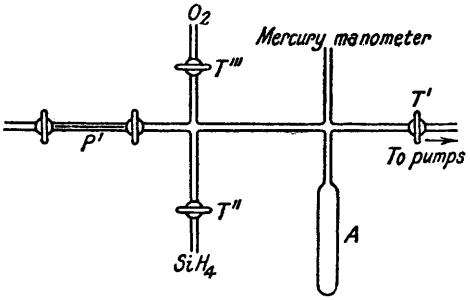
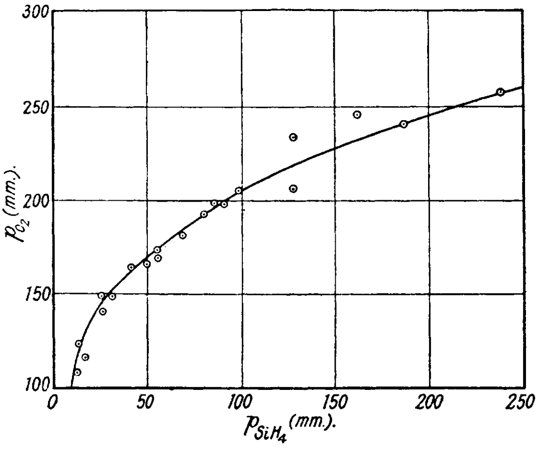


FIG. 5.



The Upper Explosion Limit.—The apparatus used in all observations on the upper explosion limit is shown in Fig. 4. The reaction bulb *A* was a cylindrical tube 10 cm. long and 1—2 cm. in diameter. The experiments were carried out as follows. The system was evacuated to a pressure less than 10^{-2} mm., the tap *T'* being then closed, and silane admitted through *T''* to the required pressure, which was read on the mercury manometer; *A* was then cooled in liquid nitrogen, and oxygen admitted through *T'''* to a pressure somewhat less than that required in the final mixture. The silane was allowed to vaporise, and additional oxygen was added to give the required mixture, 10—20 mins. being allowed for mixing. *A* was surrounded with a cylinder of copper gauze in case of violent explosions, and immersed, to a fixed mark, in a bath of boiling water. The pressure was reduced at the rate of 1 mm. in 3—8 secs. by opening the tap *T'* slightly, and was read at the instant of explosion. The inside of the apparatus became coated with a thin film of silica after the first explosion. Between successive observations, the apparatus was filled with dry air, heated with a luminous flame, and evacuated. In this way a reproducibility of ± 5 mm. was obtainable in successive readings with a constant ratio of the reactants. Readings in a clean tube were always erratic, and were not used.

A typical series of values for the partial pressures of silane and oxygen at the upper explosion limit (p_K) obtained at 100° is tabulated below.

p_{SiH_4} (cm.)	23·9	18·7	9·9	8·0	5·5	3·15	2·60	1·65
p_{O_2} (cm.)	25·6	23·9	20·4	19·2	17·4	14·85	14·0	11·65
p_K (cm.)	49·5	42·6	30·3	27·2	22·9	18·0	16·60	13·3
p_{SiH_4}/p_{O_2}	0·935	0·783	0·485	0·417	0·316	0·212	0·186	0·142

These results are shown in Fig. 5. On plotting the ratio p_{SiH_4}/p_{O_2} against p_K, a linear relationship is observed except at the lowest silane pressure, where there is a divergence. The relation is expressed by the equation $p_K = 436 p_{SiH_4}/p_{O_2} + 88$. A theoretical expression of the same form is deduced later (p. 1189). By comparison of the constants with those in the above equation certain reaction probabilities are deduced. The value of p_K was not changed when the tube diameter was varied between 1 cm. and 2·2 cm., in contrast to the effect of vessel diameter at the lower limit.

FIG. 6.

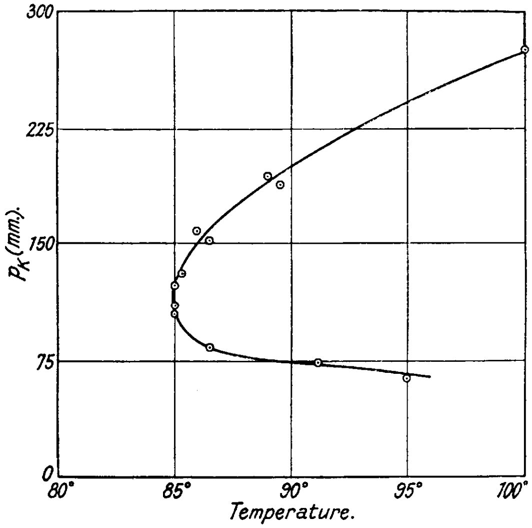
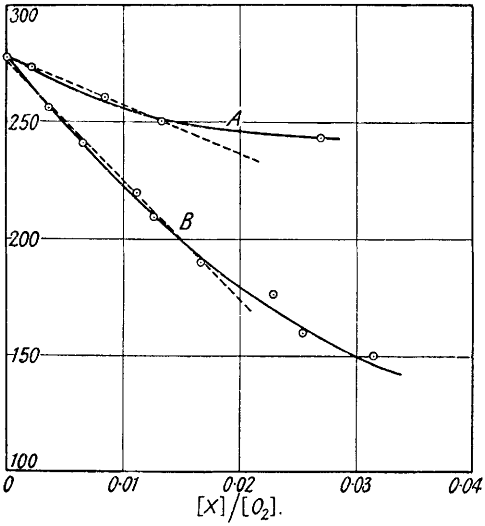


FIG. 7.



Influence of inhibitor on upper limit : A, sulphur dioxide. B, ethylene.

Influence of Temperature on the Upper Critical Pressure.—The influence of temperature was studied with a mixture containing 30% of silane. In each experiment this mixture was prepared, as already described, at a total pressure below the upper critical pressure for the mixture at 100°. *A* was immersed in a stirred water-bath at about 60°, and the temperature was raised slowly, and read at the instant when the mixture exploded. The results of a series of such measurements for different initial pressures are depicted in Fig. 6. The curve shows that a 30% silane mixture will not ignite spontaneously on reduction of pressure if the temperature is below 84°. It was also established that the higher the percentage of silane in a mixture at a given total pressure, the lower is the temperature at which it will ignite spontaneously; *e.g.*, mixtures with 70% of silane exploded in the process of mixing the two gases at 0°.

Influence of Inert Gas at the Upper Critical Pressure.—The effect of nitrogen and of helium on the upper critical pressure was examined by keeping the ratio of silane to oxygen constant and studying the variation of the critical pressure with the percentage of inert gas added. The mixture was made up as already described, the inert gas being added last. All observations were made at 100°. Results with nitrogen as diluent are tabulated below. The value of p_K is the sum of the pressures of silane, oxygen, and nitrogen at the limit. Although the limiting pressure is slightly raised owing to the presence of nitrogen, the actual pressures of silane and oxygen at the limit are much reduced.

$SiH_4 : O_2 = 1 : 5$.				$SiH_4 : O_2 = 3 : 10$.			
N_2, %.	p_K (cm.).	N_2, %.	p_K (cm.).	N_2, %.	p_K (cm.).	N_2, %.	p_K (cm.).
0	20·0	30·5	22·2	0	27·7	28·7	28·8
26	22·15	42	24·1	27·9	28·0	43·1	31·7

In experiments with helium, a silane : oxygen ratio of 1 : 5 was used. Addition of 13·6% of helium raised the critical pressure from 20·0 to 20·5 cm., while 23·0% of helium gave a value of 21·3 cm. The effect on the total pressure is evidently very small both for nitrogen and for helium. The diluent gas rendered the explosion very much weaker, and in the presence of greater amounts of nitrogen than those recorded above there was no explosion on reducing the pressure. Also the reproducibility was much poorer than for the corresponding experiments without inert gas present.

The Slow Reaction.—The possibility of there being a slow reaction above the upper explosive limit was examined in the following experiments. Two oxygen–silane mixtures, containing severally 30·8 and 30% of silane, were sealed up in bulbs in an all-glass apparatus with a mercury manometer. The first of these bulbs showed no change in pressure after 20 days at the room temperature. It was then heated at 70° ± 5° for 12 days, after which the pressure had fallen by 2 mm. (total pressure 43·3 cm.); and after 35 days it had fallen by only 5 mm. The pressure in the second bulb remained constant to ± 1 mm. during 67 days at room temperature. These experiments indicate an exceedingly slow reaction above the limit. The absence of any acceleration of the reaction rate at pressures just greater than the limit was proved as follows. With the apparatus and method already described for the study of the upper limit, a 20% silane mixture was kept at 1—2 cm. above the explosive limit at 100° for 4—6 hours. The total fall in pressure during this time was 1—2 mm., and on further reducing the pressure, explosion occurred at the expected point. A series of such experiments showed that a very slight reaction takes place above the limit, and demonstrated the extreme suddenness of the transition from the slow to the explosive reaction.

Effect of Inhibitors on the Upper Limit.—In these experiments a constant silane : oxygen ratio of 3 : 7 was again employed. The two inhibitors studied in detail were ethylene and sulphur dioxide, which were stored in reservoirs sealed on to the apparatus previously described (Fig. 4). They were measured into the tube *A* by means of a calibrated capillary gas pipette (*P'*). A known amount of silane was first admitted into the reaction tube *A*, and frozen out by cooling *A* in liquid nitrogen. The inhibitor was then added from the pipette, and finally oxygen was added and adjusted to the required pressure. The upper explosion pressure was then determined for different amounts of inhibitor. Reproducible results were obtained both with sulphur dioxide and with ethylene, the reaction vessel being heated and pumped out between successive experiments. The results are shown in Fig. 7, where the critical pressures, p_K, are plotted as ordinates, and the ratios of the pressure of ethylene or sulphur dioxide to that of oxygen as abscissæ. The results show that the critical explosion pressure is lowered by the addition of small amounts of either of these substances. The first additions of inhibitor are the most effective, and each curve has a tendency to flatten at higher concentrations. These results are discussed on p. 1189. Qualitative measurements showed that vapours of many organic substances such as benzene, ethyl iodide, chloroform, acetone, and ethyl alcohol also lower the upper critical pressure.

DISCUSSION.

The results recorded show that the oxidation of silane resembles that of phosphorus, phosphine, etc. The upper and lower critical pressures, the effect of diluent gas and of vessel dimensions on the lower critical limit, and that of inhibitors on the upper critical limit are all well-known characteristics of branching chain reactions. This type of reaction has been interpreted theoretically by Semenoff (*op. cit.*, Chaps. 1—3), and his method of treatment is followed below.

There is at present only very slight experimental evidence as to the nature of the active centres by which the chains are propagated. If one assumes that oxygen atoms are responsible for initiating the oxidation, the following scheme is possible, though speculative. It will account satisfactorily for the experimental results.

$$\text{Primary reactions} \begin{cases} SiH_4 + O = SiH_2 + H_2O & \quad \ldots\ldots \quad (a) \\ SiH_2 + O_2 = SiH_2O + O & \quad \ldots\ldots \quad (b) \end{cases}$$

followed by the secondary reactions :

$$SiH_2O + O_2 = SiH_2O_2 + O \quad \ldots\ldots\ldots \quad (c)$$

$$SiH_2O_2 + O_2 = SiO_2 + H_2O + O \quad \ldots\ldots\ldots \quad (d)$$

The reaction $SiH_4 + 2O_2 = SiO_2 + 2H_2O$ is exothermic to the extent of 324 kg.-cals. The exact thermal data for the above equations are not available, but they are very probably all exothermic. The isolation of polymerised SiH_2 by Schwarz (*Z. anorg. Chem.*, 1935, **221**, 277) strengthens the hypothesis that SiH_2 is an intermediate in the oxidation. Stock and Somieski (*loc. cit.*) have also isolated a compound with the approximate formula SiH_2O in the process of incomplete combustion. The inhibiting effect of easily oxidisable compounds is evidence for the existence of peroxides or oxygen atoms during the oxidation.

It has already been shown (p. 1184) that the results at the lower limit obey a relationship connecting the tube diameter and the partial pressures of the reactants, which would be expected for a branching chain reaction in which deactivation occurs only at the walls. From these measurements, the chain length can be calculated (Semenoff, *op. cit.*, p. 174), and from the results for the 1-cm. tube, on the assumption that 1% of the collisions between an oxygen atom and a silane molecule are fruitful, the chain length is found to be 2, and the probability of branching 1 in 6.

The general relationship deduced by Semenoff for inflammation is :

$$(\delta - \beta) \times \nu_1 = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

where β is the probability that a chain will be broken at any particular link in the gas phase, δ is the probability that branching will occur at any given link, and ν_1 is the average length of the primary chain corresponding to all chains being broken on the wall. Let us suppose that branching can occur in two ways: (i) Branching (as in equations *b*, *c*, and *d*) taking place on the wall, with a probability δ_1 corresponding to any given link; (ii) collisions of the type $O + O_2 = O + O_2^*$, where the oxygen atom with excess energy imparts sufficient of it to the oxygen molecule to render such subsequent reactions as $SiH_4 + O_2^* = SiH_2 + O + H_2O$ possible. If, on the average, q collisions between an oxygen atom and a silane molecule (equation *a*) are necessary to ensure reaction, then during this time interval Δt the oxygen atom will suffer $q[O_2]/[SiH_4]$ collisions with an oxygen molecule. If ε is the chance that the latter shall involve reaction, then the probability δ_2 of branching occurring in this manner is $q\varepsilon[O_2]/[SiH_4]$. Finally, $\delta = \delta_1 + \delta_2$.

For deactivation in the gas phase by three-body collisions, we have $O + O_2 + M = O_3 + M$, where M is any third molecule, which may be oxygen, silane, inert gas, or inhibitor. During the same time Δt as above, the oxygen atom undergoes $4 \times 10^{-6} . q[O_2][M]/[SiH_4]$ collisions of this type, where 4×10^{-6} is the ratio of the number of ternary to the number of binary collisions at a pressure of 1 mm. If μ is the probability of this reaction occurring, then :

$$\beta_1 = q \cdot \frac{[O_2]}{[SiH_4]} \times 4 \times 10^{-6} \times \sum_{r=1}^{n} \mu_r[M]$$

where β_1 is the probability of chain-breaking by three-body collisions involving an oxygen atom. The summation represents the concentrations of different third molecules M, and μ_r is the probability of the three-body process occurring for the different species of M. A collision of an oxygen atom with a molecule of an easily oxidisable substance X may result in reaction of the type $O + X = OX$, giving $\beta_2 = q\rho[X]/[SiH_4]$, where ρ is the probability of such a collision being fruitful. Then $\beta = \beta_1 + \beta_2$.

Finally, substituting in equation (*e*), and putting ν_1 equal to $kd^2[O_2][SiH_4]$, we get

$$\delta_1 + q\varepsilon\frac{[O_2]}{[SiH_4]} - 4 \times 10^{-6} q \frac{[O_2]}{[SiH_4]} \sum_{r=1}^{n} \mu_r[M] - q\rho\frac{[X]}{[SiH_4]} = \frac{\text{const.}}{d^2[O_2][SiH_4]}$$

On rearrangement, we get :

$$[SiH_4][O_2] + \frac{q\varepsilon}{\delta_1}[O_2]^2 - 4 \times 10^{-6}\frac{q}{\delta_1}[O_2]^2 \sum_{r=1}^{n} \mu_r[M] - \frac{q\rho}{\delta_1}[X][O_2] = \frac{K}{d^2\delta_1}$$

Now $\frac{K}{d^2\delta_1}$ is the constant in the lower-limit formula and may be neglected in comparison with the other terms at the upper limit. In the absence of inert gas and inhibitor, the equation becomes

$$[\mathrm{SiH_4}][\mathrm{O_2}] + \frac{q\varepsilon}{\delta_1}[\mathrm{O_2}]^2 - 4 \times 10^{-6}\frac{q}{\delta_1}[\mathrm{O_2}]^2\{\mu_1[\mathrm{O_2}] + \mu_2[\mathrm{SiH_4}]\} = 0$$

Putting $\mu_1 = \mu_2 = \mu$ and rearranging we get

$$\frac{\delta_1}{\mu q\,.\,4 \times 10^{-6}}\frac{[\mathrm{SiH_4}]}{[\mathrm{O_2}]} + \frac{\varepsilon}{\mu\,.\,4 \times 10^{-6}} = [\mathrm{O_2}] + [\mathrm{SiH_4}]$$

whence, by comparison with the equation expressing the experimental results on p. 1186, we find that $\delta_1/(\mu q \times 4 \times 10^{-6}) = 436$ and $\varepsilon/(\mu \times 4 \times 10^{-6}) = 88$. With inert gas in the mixture, the predicted relationship becomes

$$\frac{\mu_3}{\mu}[\mathrm{N_2}] = 436\frac{[\mathrm{SiH_4}]}{[\mathrm{O_2}]} + 88 - [\mathrm{O_2}]\left\{1 + \frac{[\mathrm{SiH_4}]}{[\mathrm{O_2}]}\right\}$$

Thus for a given ratio we may calculate from experimental data a value for μ_3/μ, which expresses the ratio of the efficiency of nitrogen or helium in bringing about the three-body reaction $O + O_2 + M = O_3 + M$ compared with that of silane or oxygen. The values of the ratio vary from 0·57 to 0·88. If the ratio were unity, nitrogen and helium would be without effect on the upper critical limit. The following table summarises the results.

$SiH_4 : O_2 = 3 : 7$.		$SiH_4 : O_2 = 1 : 4$.		$SiH_4 : O_2 = 1 : 4$.	
N, %.	μ_3/μ.	N, %.	μ_3/μ.	He, %.	μ_3/μ.
43·1	0·72	42·0	0·58	23·0	0·88
28·7	0·83	30·5	0·62	13·6	0·68

With inhibitor present in the gas mixture, the theoretical relationship becomes

$$\dot{p}_{\mathrm{K}} = [\mathrm{O_2}] + [\mathrm{SiH_4}] + [\mathrm{X}] = 436[\mathrm{SiH_4}]/[\mathrm{O_2}] + 88 - 436q\rho[\mathrm{X}]/\delta_1[\mathrm{O_2}] \quad \text{if} \quad \mu_4 = \mu.$$

From this equation it follows that the relation between the upper critical pressure and the ratio $[X]/[O_2]$ should be linear when the ratio $[SiH_4]/[O_2]$ is kept constant. That this is actually the case is shown by Fig. 7, departure from the linear relationship only becoming appreciable when the concentration of the inhibitor is high and the error due to the approximation introduced by putting $\mu_4 = \mu$ becomes appreciable.

From the values obtained for the constants in the above equations, it is possible to calculate numerical values for the probabilities of certain reactions occurring on collision. If μ is put equal to 1×10^{-1} (the value obtained by Semenoff for phosphine oxidation) and $q = 100$ (arbitrarily), the value of δ_1 is found to be 1/57. The values of $\rho_{C_2H_4}$ and ρ_{SO_2}, these being the probabilities of reaction of an oxygen atom on collision with a molecule of ethylene or sulphur dioxide, are 2×10^{-3} and $0{\cdot}77 \times 10^{-3}$ respectively. These values are in general agreement with those obtained in other reactions (Melville, *Trans. Faraday Soc.*, 1932, **28**, 313). The value of ε is found to be $3{\cdot}5 \times 10^{-5}$.

These observations are being extended to other hydrides of silicon in order to obtain further evidence by which to test the reaction mechanism now suggested.

SUMMARY.

(1) In the oxidation of silane to silica and water, both lower and upper critical oxidation limits have been observed.

(2) The effects of the dimensions of the reaction vessel and the presence of nitrogen on the lower limit, and that of temperature, diluent gas (nitrogen or helium), and of inhibitor (sulphur dioxide or ethylene) on the upper limit, have been studied. These observations are consistent with the process being a branching chain reaction.

(3) The results are discussed on the generalised Semenoff theory of chain reactions.

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