564. *The Reaction between Diborane and Oxygen.*

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The reaction between diborane and oxygen has been studied at temperatures between 120° and 210° c. There is a low-pressure explosion region and most of the work has been concerned with measuring second-limit pressures and the effect on these of composition, of the size and surface of the vessel, and of added inert gases, hydrogen, and organic vapours. First limits and reaction rates were also studied, as well as the explosion of mixtures containing small proportions of oxygen. It was concluded that the mechanism proposed by Price is essentially correct, though the effect of the surface seems to be more important than he supposed. The radical involved in the branching–breaking competition is an oxidising one, possibly BH_3O_2. The mechanism has been examined quantitatively.

EXPLOSION limits for mixtures of diborane and oxygen at temperatures in the neighbourhood of 150—200° c have been studied by Price,[1] Whatley and Pease,[2] Roth and Bauer,[3] and Snyder and Bauer.[4] They have shown that the reaction proceeds by a branching-chain mechanism, but as regards the detailed results and interpretation there is considerable disagreement. We therefore examined this reaction, in the hope of resolving the differences and also of obtaining more knowledge about the mechanism of the reaction.

Price, using admission and withdrawal methods, showed the existence of first and second explosion limits. Roth and Bauer, on the other hand, determined the limits by using the heating method; a thermocouple on the side of the reaction vessel recorded the temperature as an oil-bath was raised around the vessel to heat it rapidly. Price measured pressure with a mercury manometer, but Roth and Bauer excluded mercury and used a bellows manometer. Price degassed his reaction vessel at room temperature, using only a mechanical pump, but Roth and Bauer employed a diffusion pump, the vessel being kept at the reaction temperature during the pumping. The results of Price and of Roth and Bauer are compared in Fig. 1. It is generally agreed that both limits are at low pressures. There was fair agreement regarding the first limit but not regarding the second; Price found a crossing of his first- and second-limit graphs. Roth and Bauer determined second limits at one temperature, using Price's degassing procedure, and obtained similar results to his. When Price's pumping procedure was used, Roth and Bauer observed a green glow on admitting oxygen to the heated reaction vessel, indicating that oxidisable boron material had not been removed under these conditions. There was agreement that the second limit was independent of vessel size. Price claimed that this was true for the first limit also, concluding that, in the neighbourhood of this first limit, both branching and breaking processes occur at the wall. Both sets of experiments included an investigation of the effects of changing the composition of the mixture and of adding nitrogen and hydrogen. Roth and Bauer also added argon and helium and found that these gases, as well as nitrogen, exerted the normal inert-gas effect at the second limit. They found that hydrogen acted as a promoter when small amounts were added but as an inhibitor when larger quantities were used.

Different interpretations were offered by Price and by Roth and Bauer. Price concluded from his results for the second limit that the chain-branching and -breaking processes occurred in the gas phase. At a particular temperature the data could be represented by:

$$ap_B + bp_O + cp_N + dp_H + k = 0$$

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[1] Price, *J. Amer. Chem. Soc.*, 1950, **72**, 5361.

[2] Whatley and Pease, *J. Amer. Chem. Soc.*. 1954. **76**. 1997.

[3] Roth and Bauer, Fifth Symposium on Combustion, Reinhold Publ. Corp., New York, 1955, p. 710; *J. Phys. Chem.*, 1956, **60**, 639.

[4] Snyder, *Diss. Abs.*, 1959, **19**, 239.

where $p_{\rm B}$, $p_{\rm O}$, $p_{\rm N}$, and $p_{\rm H}$ are the partial pressures of B_2H_6, O_2, N_2, and H_2. At 180° he found $b/a = -0{\cdot}9$, $c/a = -0{\cdot}6$, $d/a = -0{\cdot}6$, $k/a = 9{\cdot}0$. From the above signs he concluded that the k and the B_2H_6 terms ($ap_{\rm B}$) represented branching reactions and that the O_2, N_2, and H_2 terms represented breaking ones. It may be supposed that the k and B_2H_6 terms correspond respectively either to first- and second-order processes or to second- and third-order ones. Price favoured the former, in which the branching processes are second-order. If X is the active species then the branching processes suggested by Price are

$$\left.\begin{array}{l} \mathrm{X} + \mathrm{B_2H_6} \longrightarrow \\ \mathrm{X} \qquad\quad\;\; \longrightarrow \end{array}\right\} \text{ Branching,}$$

and the breaking processes are

$$\left.\begin{array}{l} \mathrm{X} + \mathrm{O_2} \longrightarrow \\ \mathrm{X} + \mathrm{N_2} \longrightarrow \\ \mathrm{X} + \mathrm{B_2H_6} \longrightarrow \end{array}\right\} \text{ Breaking.}$$

and possibly

Corresponding processes can be written for a mechansim in which the branching processes are of the second and third order.

Roth and Bauer discarded Price's interpretation of the opposite effects of diborane and oxygen on the pressure of the second limit. In their discussion they did not examine in detail the effect of composition on the limit at a fixed temperature but analysed, for a fixed limit pressure, the effect of composition on limit temperature. They found that if they made certain assumptions they could account for this with a mechanism similar to that of the hydrogen–oxygen reaction in which BH_3 in their mechanism was substituted for H in the now generally accepted branching cycle of the hydrogen–oxygen reaction. They postulated also the breaking reaction

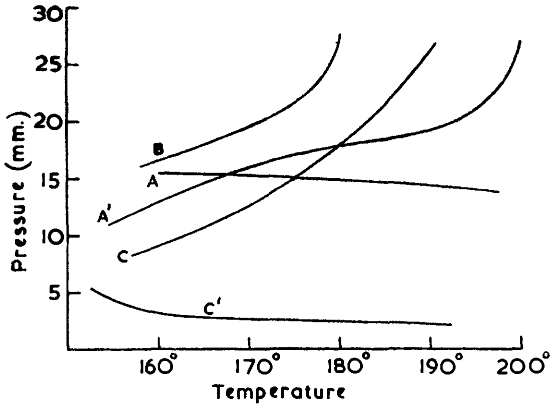

FIG. 1. Comparison of the results of (A, A') Price,[1] (A, B) Roth and Bauer,[3] and (C, C') ourselves for the first and second explosion limits for 3 : 1 O_2–B_2H_6 mixtures.

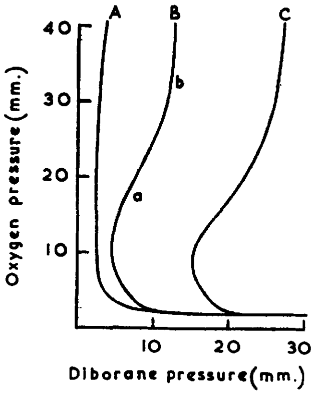

FIG. 2. The results of Whatley and Pease.[2]

A, 165°; B, 145°; C, 120°.

$$BH_3 + O_2 + M \longrightarrow HBO_2 + H_2 + M$$

analogous to

$$H + O_2 + M \longrightarrow HO_2 + M$$

However, since their mechanism does not account for the effect of composition on the limit pressure at a fixed temperature, it must be regarded as unsatisfactory. Moreover, there is no evidence that the branching cycle resembles that of the hydrogen–oxygen reaction. In addition, it is questionable whether it is worthwhile, at the present time, to propose such a detailed mechanism as Roth and Bauer have done since there is virtually no *direct* evidence as to the nature of the intermediates and formulation of such a detailed mechanism in a complex system of this type purely on the basis of kinetic evidence cannot be justified.

Whatley and Pease studied the explosion limits of diborane–oxygen mixtures between 120° and 165° c. They allowed induction periods of up to 1000 sec. for explosion to occur and plotted limit pressures of diborane and oxygen for various temperatures. Their results are shown in Fig. 2. It will be seen that the low-pressure explosion region, unlike that in the hydrogen–oxygen reaction, does not form a closed area in Fig. 2 but merges into the region of the third limit. Whatley and Pease also found that diborane and oxygen had opposite effects at the second limit. That is, the part of the line for 145° which lies between a and b, and represents a second limit in terms of total pressure, is a limit at which explosion would occur on lowering the oxygen pressure at a fixed diborane pressure, but on *raising* the diborane pressure at a fixed oxygen pressure. These curves illustrate clearly how different this reaction is from the hydrogen–oxygen reaction. We have obtained curves which are similar in form to those of Whatley and Pease, though some of our experiments are at higher temperatures and none allows induction periods of 1000 sec. Whatley and Pease did not propose a mechanism.

Fehlner and Strong [5] have investigated the action of oxygen atoms on diborane at 25° and 100° c. Initially hydrogen, B_4H_{10}, B_5H_9, and a white solid of empirical formula HBO are formed. It appears that the oxygen atoms initiate a sequence of reactions analogous to those occurring during pyrolysis of diborane. It is difficult to assess the degree of relevance of these observations to those obtained for the diborane–oxygen reaction at 150—200° c because there is no clear evidence for the presence of oxygen atoms in the systems studied by us.

EXPERIMENTAL

The apparatus was conventional, consisting of a reaction vessel, a vacuum-line with storage vessels, and a rotary oil pump backing a mercury-diffusion pump. Diborane, prepared and purified by a method described elsewhere,[6] was stored in a 500-c.c. Pyrex bulb fitted with a mercury cut-off valve. The other gases were stored in other bulbs having ordinary, greased vacuum-taps. Mixtures of gases for introduction to the reaction vessel were made up in bulbs in which the pressures were measured by a mercury manometer. Mixtures could also be made directly in the reaction vessel. A flame trap was fitted to the diborane line to prevent a flame in the reaction vessel spreading back to the main line. For most experiments, the Pyrex reaction vessel was 4 cm. in diameter and 8 cm. long, having hemispherical ends, but a narrower one, 2 cm. in diameter, was also used. It was joined to the main line through a waxed B7 cone for ease of removal for cleaning. The final leads to the reaction vessel were of capiliary tubing to reduce the dead space, and pressures were measured with a mercury manometer. The contents could be pumped from the reaction vessel through a fine interchangeable capillary, so that the pumping speed could be controlled when the withdrawal method was being used for the determination of the second limit. The reaction vessel was heated in a thermostat-controlled bath containing Silicone oil. The oil was stirred vigorously and the bath could be raised and lowered relative to the fixed reaction vessel, so that the latter could be heated quickly by raising the bath rapidly around it.

Oxygen, nitrogen, hydrogen, and helium were obtained from cylinders. The oxygen was condensed in a trap cooled in liquid air, and the middle fraction was used. The hydrogen and nitrogen were taken from full cylinders when the pressure was >100 atm., so that the moisture content would be low. The helium, which was kindly given to us by the Clarendon Laboratory, was taken from a cylinder at 200 lb./sq. in. It contained a little hydrogen but no other impurity. The B_5H_9 was kindly supplied to us by Explosives Research and Development Establishment, Waltham Abbey, and was described as spectroscopically pure.

Mixtures were always made up at fairly high pressure (>100 mm. in the mixing vessel and

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[5] Fehlner and Strong, *J. Phys. Chem.*, 1960, **64**, 1522.

[6] Danby, Gobbett, and Linnett, *J.*, 1962, 2076.

>50 mm. in the reaction vessel) to ensure that the compositions were known accurately. When it was necessary to make small additions to a mixture, the material was measured in the small volume of the vacuum-line and partitioned into the relatively large volume of the mixing vessel.

The first limit was determined both by the admission method and by Roth and Bauer's heating method. Admission was carried out, first, by allowing the mixture to flow into the reaction vessel, the pressure of the latter being followed on its manometer. Later, to obtain greater accuracy, a mixture of known pressure was put into the flame-trap space and allowed to flow into the reaction vessel until explosion occurred. The pressure drop in the flame-trap space was related to the pressure in the reaction vessel by calibration with nitrogen. When the heating method was used the vessel was heated by raising the oil-bath; the limit was then bracketed, one minute being allowed for heating of the vessel.

Second limits were determined by the withdrawal method. The mixture was admitted to, or made up in, the reaction vessel at room temperature. The oil-bath was raised and 90 sec. were allowed for the vessel to reach the bath-temperature. The gas was then withdrawn as quickly as was consistent with obtaining a satisfactory determination of the limit.

Combustion of diborane produces a solid deposit on the walls of the reaction vessel. Like Roth and Bauer, we found that incomplete degassing lowered the second limit. It also seemed that the accumulation of a heavy coating after many runs had the same effect. It was necessary therefore to remove the deposit periodically. It was usually possible to do this with methanol, followed by several washings with distilled water, but sometimes chromic acid had to be used (also followed by distilled water). The results obtained on using a vessel which had just been cleaned were erratic; so, after being cleaned, the inner surface was coated by inducing two or three explosions with small amounts of mixture before recorded runs were started. When the coating was not too heavy, consistent results were obtained after pumping for at least 15 min. at the reaction temperature. For second-limit determinations, degassing was continued while the vessel was cooling to room temperature.

The extent to which pre-reaction is important in determination of the limits must be considered. At the second limit there seemed to be little difficulty when the delay before withdrawal was 90 sec., this being our standard procedure. With delays greater than 3 min. the limit was depressed a little. At the first limit, the results did depend on the rate of admission and sometimes a glow could be seen as the first portions flowed in. When this happened the explosion occurred at a higher pressure or not at all. Finally, the procedure was standardised by admitting the mixture as quickly as the reading of the manometer allowed. Most of the results for the first limits were then consistent, though not all (see Results section).

Vapour-phase Chromatography.—A few analyses of partly reacted mixtures were carried out by vapour-phase chromatography. The column had to be short (20 cm.) so as to reduce decomposition of unstable compounds. The column, 4 mm. in diameter, was packed with Celite containing 20% by weight of an involatile Silicone oil. A differential thermal-conductivity detector was used. The sample was collected by means of a large Toepler pump, and then transferred to a pipette volume. The carrier gas was nitrogen for some experiments and hydrogen for others. The peak due to B_5H_9 was identified by its retention volume, this being determined by using a known sample. The peak due to B_5H_{11} was identified from its retention volume relative to that of B_5H_9 (Littlewood[7]). B_4H_{10} was identified as a product in the hydrolysis of diborane at room temperatures and by its relative retention volume.

RESULTS

First Limit.—Because of lack of reproducibility in the results for the first limit, fifty measurements were made by the admission method with a stoicheiometric diborane–oxygen mixture containing 25% of diborane at 180°. Thirty gave results which were consistent with one another; twelve gave higher limits, and eight did not produce explosions. It appeared that the high results were obtained when admission was slow and also when the mixture glowed as it was being admitted. This suggests that the high results are obtained when there is pre-reaction; consequently, subsequent experiments were carried out with as rapid admission as possible. Careful observation showed that, when explosion occurred, there was a green glow in the middle of the vessel which developed rapidly into a flash.

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[7] A. B. Littlewood, D.Phil. Thesis, Oxford, 1957.

The limits for mixtures of diborane and oxygen in the vessel of 4 cm. diameter are shown in Fig. 3. The limit is decided primarily by the diborane pressure. A few results for the 2 cm. vessel are plotted in the same Figure. These show that the limit pressure is raised by decreasing the diameter of the vessel, as would be expected if chain branching were occurring in the gas phase and breaking at the walls. Fig. 1 shows that our first limits are at very much lower pressures than those obtained by Price and by Roth and Bauer. The addition of nitrogen lowered the first-limit pressure. For example, at 180° in the 4-cm. vessel the limit pressure for a 3 : 1 O_2–B_2H_6 mixture was found to be 3·2 mm. For a 3 : 1 : 1 O_2–B_2H_6–N_2 mixture it was 2 mm. For other similar mixtures results of the same kind were obtained, but when larger amounts of nitrogen were added (forming, say, more than half the total mixture) glows were observed and the mixture did not explode till at much higher pressures. The occurrence of these glows suggested that, in these cases, pre-reaction occurred with a resultant raising of the limit.

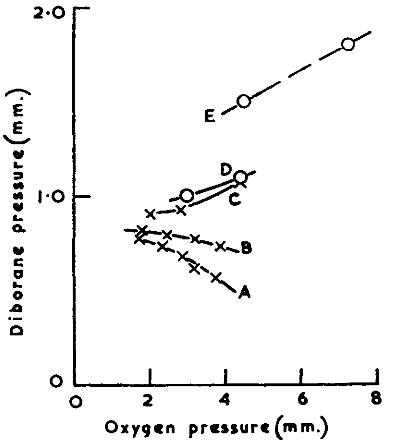


FIG. 3. Partial pressures at the first explosion limit (pipette method).

4-cm. vessel, (A) 190°, (B) 180°, (C) 170°; 2-cm. vessel, (D) 180°, (E) 170°.

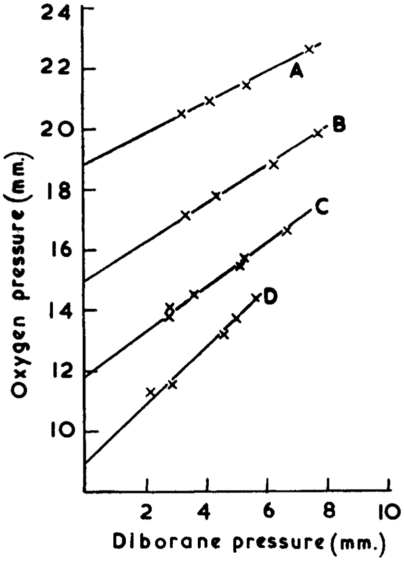


FIG. 4. Partial pressures at the second explosion limit.

A, 195°; B, 190°; C, 185°; D, 180°.

In order to see whether the nature of the vessel surface had an effect, it was coated with an incompletely oxidised boron surface by exploding in it several 1 : 9 mixtures of diborane and oxygen. After this treatment no first-limit explosion could be obtained, even up to 25 mm., showing that a surface of such a low oxygen content has high chain-breaking efficiency. After three stoicheiometric mixtures (3 : 1) had been exploded in the vessel at 10 mm. pressure by using a Tesla discharge, an explosion could be obtained and subsequent measurements gave progressively lower limits, the results approaching the " normal " value.

Limits obtained by the heating method were a little higher than those obtained by the admission method. This is probably a consequence of pre-reaction.

Second Limit.—The first experiments were made with diborane which contained a little ethyl fluoride.[6] Second limits were determined by making mixtures with oxygen in a mixing vessel. These were then passed into the reaction vessel. Consistent results were obtained. But with the purer diborane, freed from ethyl fluoride, the results became inconsistent when the same procedure was used. The ethyl fluoride had apparently stabilised the diborane–oxygen mixtures during storage. In its absence, then, mixtures underwent a reaction which caused a lowering of the second-limit pressure. Since no means could be found of achieving reproducibility after premixing, the procedure was changed and mixtures were made up in the

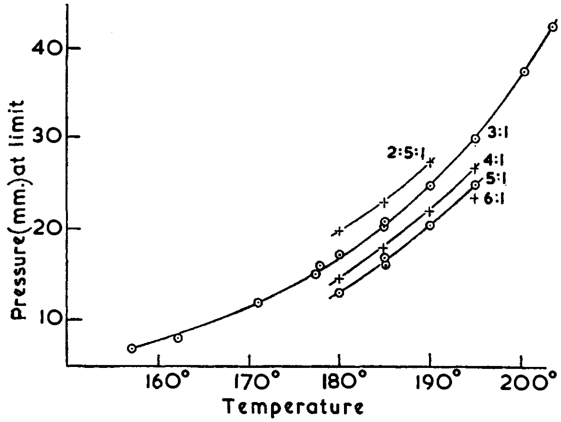
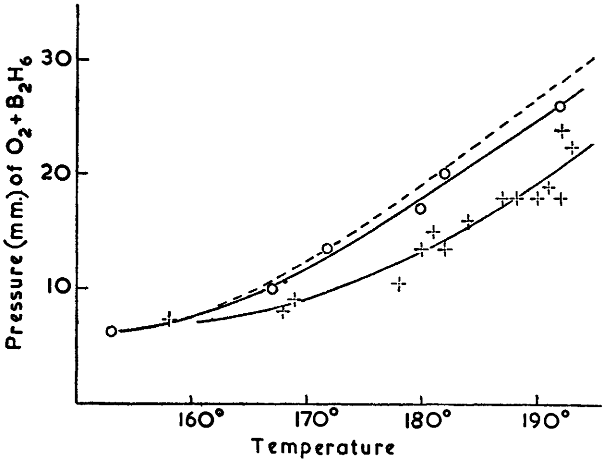


FIG. 5. Variation of the second limit with temperature for different mixture compositions (ratios marked are $O_2 : B_2H_6$).

FIG. 6. Effect of nitrogen on the partial pressure of diborane and oxygen at the second limit for 3 : 1 O_2–B_2H_6 mixtures. Percentages of added gas, as percentages of the whole gas mixtures, are: – – – no nitrogen; O—O nitrogen 10%; +—+ nitrogen 20%.



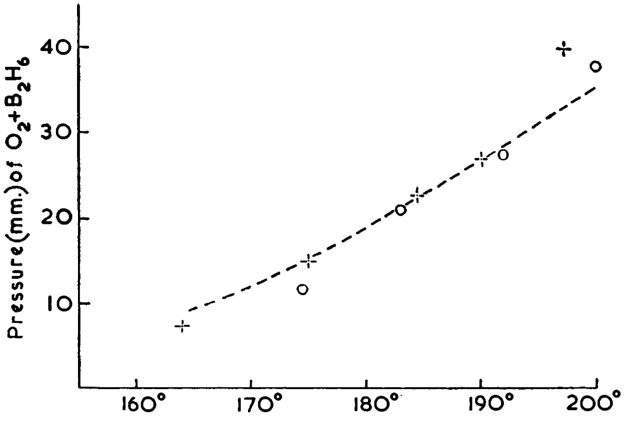


FIG. 7. Effect of helium on the partial pressure of diborane and oxygen at the second limit for 3 : 1 O_2–B_2H_6 mixtures. Percentages of added gas, as percentages of the whole gas mixture, are: – – – no helium; O—O helium 5%; +—+ helium 10%.

reaction vessel immediately before use. This gave satisfactory results and limits were reproducible over long periods.

Results for the effect of composition are shown at 180°, 185°, 190°, and 195° in Fig. 4, and a complete curve of limit pressure against temperature for a 3 : 1 mixture is given in Fig. 5. The results in Fig. 4 show the difference of this reaction from that of hydrogen with oxygen. They resemble Price's results, which were also obtained by Roth and Bauer but subsequently ignored by them.

The effect of adding nitrogen to a 3 : 1 mixture is shown in Fig. 6. With 10% of nitrogen the total limit pressure is hardly affected but with 20% there is a marked lowering. For both mixtures the partial pressure of the reactant mixture is lowered, suggesting that nitrogen exerts a normal inert-gas second-limit effect. Similar results for helium are shown in Fig. 7. As regards the third-body deactivating effect, helium would be expected to be less efficient per collision than oxygen, but to make more collisions per unit time with an active species. This might be the explanation of the change in behaviour with temperature, though there may also be some additional effect. The results obtained by adding hydrogen which are shown in Fig. 8 are complicated. However, at the lower temperatures the limits are lowered and this may be, at any rate in part, a normal inert-gas effect. At the higher pressures small amounts raise the limit, which may mean that at these temperatures one of the active chain species reacts with hydrogen in such a way as to enhance chain branching.

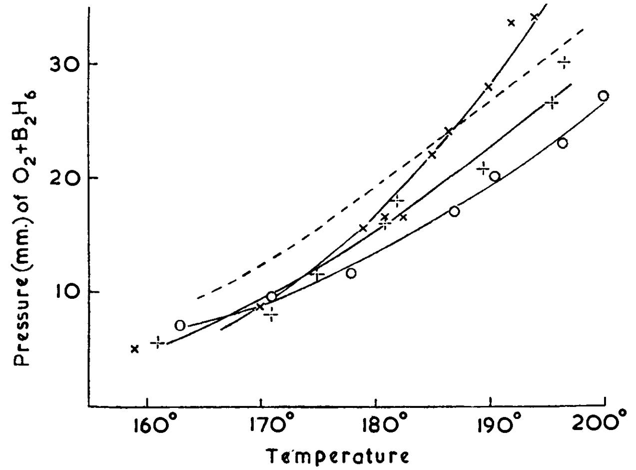


FIG. 8. Effect of hydrogen on the partial pressure of diborane and oxygen at the second limit for 3 : 1 O_2–B_2H_6 mixtures. Percentages of added gas, as percentages of the whole gas mixture, are: – – – no hydrogen; × hydrogen 3·3%; + hydrogen 15%; ○ hydrogen 20%.

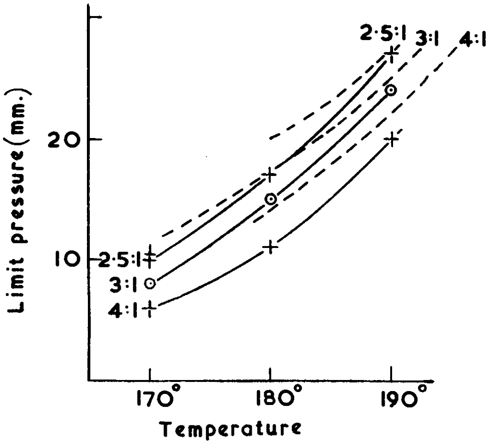


FIG. 9. Effect of vessel size on the second limit for O_2–B_2H_6 mixtures noted on the curves (right-hand set for 4-cm. vessel; left-hand set for 2-cm. vessel).

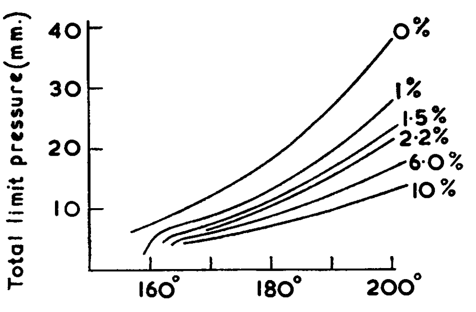


FIG. 10. Effect of ethyl fluoride on the second limit for 3 : 1 O_2–B_2H_6 mixtures. (Figures on the curves are percentages of C_2H_5F present.)

In addition to the experiments in the 4-cm. vessel, some measurements of second limits were made in the 2-cm. vessel. These are compared in Fig. 9. The limits are lower in the smaller vessel, the lowering being greater at lower temperatures when the limit pressure is lower. This suggests that some first-limit chain-breaking effect still occurs at the second limit, which is not surprising since the pressures are low (10—20 mm.).

At the start of this work, we were unaware that the diborane we had made and were using contained ethyl fluoride.[6] However, as a consequence we came to study the effect of ethyl fluoride on the limit and the results are shown in Fig. 10. Ethyl fluoride depresses the limit very strongly. Further experiments in which methane, benzene, acetone, diethyl ether, n-hexane, and cyclohexane were added (0·5% of each) showed that these substances had similar effects (see Fig. 11). Presumably these organic substances exert a strong breaking effect by removing active oxidising species.

Since it had been suggested that the formation of less stable higher hydrides triggered the explosion, the effect on the second limit of adding pentaborane was examined. The results (see Fig. 12) show clearly that the presence of pentaborane does make the mixture much more explosive. It was possible to obtain explosions down to about 120°; in the absence of pentaborane the lowest explosion temperature was about 157°. This, of course, only shows that pentaborane would have a pro-explosive effect if it were produced in small quantities during the decomposition of diborane–oxygen mixtures, but it does not prove that this happens. However, it is possible that the production of pentaborane, or some other higher hydride, in mixtures of diborane and oxygen in the mixing volume at room temperature was the cause of the initial lack of reproducibility of the second limits when pure diborane was used. If so, ethyl fluoride apparently prevents the formation of the pentaborane or other hydride under these circumstances.

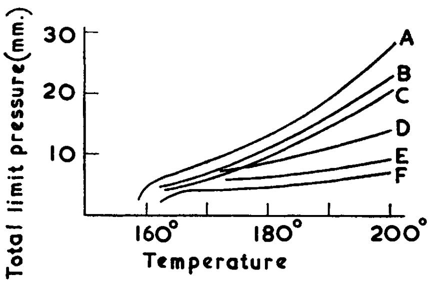


FIG. 11. Effect of organic additives on the second limit (0·5% of each added to 3 : 1 O_2–B_2H_6 mixture).

Additive: A, None; B, CH_4; C, C_6H_6; D, acetone; E, ether; F, n-hexane or cyclohexane.

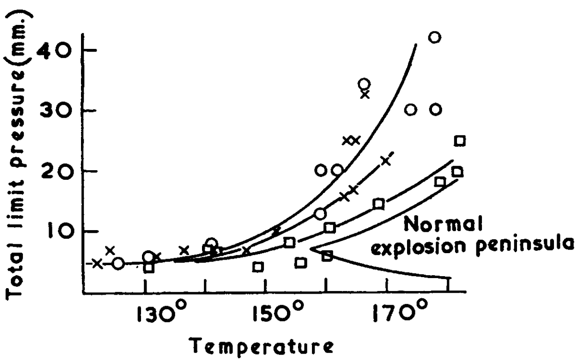


FIG. 12. Effect of pentaborane on the second limit of 3 : 1 O_2–B_2H_6 mixtures. B_5H_9 added: ○ 5·0%; × 2·5%; □ 1·25%.

Rate of Reaction.—A few measurements were made of reaction rates, at 205°, by admitting a mixture of diborane and oxygen to the cold reaction vessel, raising the oil-bath, and following the pressure change. (The diborane contained 1% of ethyl fluoride.) Observation of genuine induction periods is impossible because of the heating period (it was impossible to avoid a heating period because the addition of either gas to the other at the reaction temperature always resulted in immediate explosion). The maximum rate of pressure decrease, after the increase which resulted from heating, was taken to be a measure of the reaction rate. Two measurements were made for each mixture and agreed extremely well. The results (Table 1) show that increasing the diborane pressure at constant oxygen pressure increases the rate, while increasing the oxygen pressure at constant diborane pressure decreases the rate. This demonstrates again that diborane and oxygen have different effects on the reaction.

TABLE 1.

Partial pressure (mm.): B_2H_6	9	12	12	12	18
O_2	36	24	36	48	36
Max. rate (mm./min.)	0·62	1·56	1·37	0·72	2·12

For the slow reaction, the rate of production of hydrogen was measured by vapour-phase chromatography. This was done in order to be able to estimate the importance of the hydrolysis of the excess of diborane by water produced by oxidation; such hydrolysis would produce hydrogen. Mixtures of diborane and oxygen (1 : 3), when heated for 90 sec. at 150—190°, showed no evidence of hydrogen. This means that hydrolysis and hydrogen production cannot be an important factor when a heating period of 90 sec. is used before determination of the second limit. On the other hand, a mixture that had been heated at 190° for 10 min. was found to contain a considerable amount of hydrogen, indicating that water produced by oxidation had hydrolysed some of the excess of diborane.

Results Obtained by Vapour-phase Chromatography.—Some analyses were made in which diborane was heated alone. At 180° the reaction, indicated by the pressure change, was rapid; the main product was B_5H_9. At 110°, it was much slower and, although some pentaborane was formed, there were relatively larger amounts of B_4H_{10}. At 130° the products were more complex, and B_4H_{10}, B_5H_9, and B_5H_{11} were all observed, though after an hour the main product was B_5H_9. These results are similar to those obtained by other workers.[7]

The addition of an equal volume of nitrogen did not affect the nature of the mixtures obtained. When a 1 : 1 mixture of diborane and oxygen was heated to 145° for an hour there was no pressure change (whereas with nitrogen instead of oxygen there had been a considerable increase). Moreover, no volatile products could be detected chromatographically. However, if a mixture so treated was left at room temperature overnight, a white deposit was formed and B_4H_{10} could be detected in the gaseous products. A similar mixture which had not been heated did not show these effects overnight, so that there must have been some interaction at 145°.

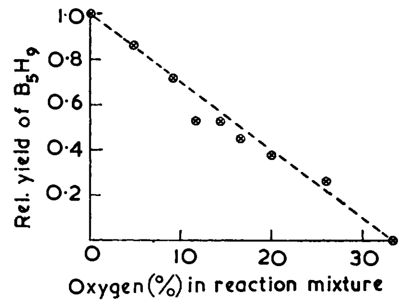


FIG. 13. Inhibition of the formation of pentaborane from diborane by oxygen.

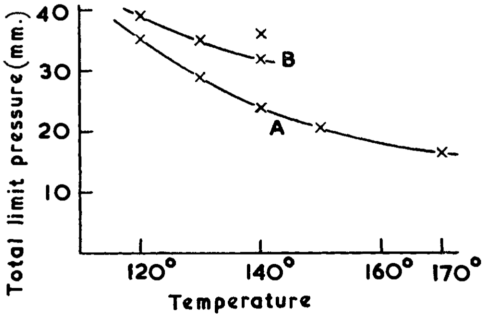


FIG. 14. Effect of temperature, composition, and vessel size on the "low oxygen content" explosion limit.

4-Cm. vessel, (A) O_2 10%, (B) O_2 5%. Point above curve B, 2-cm. vessel, O_2 10%.

Experiments were then carried out with mixtures containing small amounts (10%) of oxygen; it was found that explosions then occurred down to relatively low temperatures, as had been observed by Whatley and Pease (see below). When explosion occurred, a little pentaborane was observed in the products. An hour's heating at 110° of a mixture containing 5% of oxygen gave no detectable pyrolysis products, but heating at 135° produced a little pentaborane. A series of experiments was carried out at 150° in which diborane containing varying percentages of oxygen was heated for 40 min. and then analysed. The amounts of B_5H_9 produced (relative to that produced in the absence of oxygen) are shown in Fig. 13. The experiments with diborane containing 0—13% of oxygen were made with an initial diborane pressure of 15 mm.; those with more oxygen were made with an initial pressure of 8 mm., the results for the latter being related to that for an initial diborane pressure of 8 mm. in the absence of oxygen.

These results can be explained by supposing either that oxygen inhibits the pyrolysis of diborane and the formation of pentaborane or that it removes by oxidation the pentaborane formed by pyrolysis. If the latter, then hydrogen should be formed; but when a 1 : 1 mixture of diborane and oxygen was heated at 150° for 30 min. no hydrogen could be detected in the products. So it is evident that the pyrolysis of diborane and the formation of pentaborane are inhibited by oxygen.

The above experiments show that it is most unlikely that the explosive oxidation of diborane–oxygen mixtures containing a high proportion of oxygen involves the production of pentaborane (or any other higher hydride) as a sensitiser for the explosion.

"Low Oxygen Content" Explosion.—The limits for mixtures containing small amounts of oxygen resembled those found by Whatley and Pease.[2] A heating method was employed in determining these limits (which are of the first-limit type), a delay of 120 sec. being allowed. The effects of temperature and vessel size on the limit are shown in Fig. 14, that of composition in Fig. 15, and that of adding helium and nitrogen in Fig. 16. The first shows that the mixture becomes more explosive as the temperature is raised, Figs. 14 and 15 show that, as the amount of oxygen is increased, the limiting pressure of diborane is decreased, which is a different type of behaviour from that observed when oxygen is in excess. An attempt was made to find the effect of increasing the oxygen percentage to 30% and beyond, but this was impossible because explosions could not be obtained when the proportion of oxygen exceeded one-third.

These explosions had a different appearance from those of mixtures containing a high proportion of oxygen, giving pale blue or white flashes. At the higher oxygen percentages (15—20%) and higher temperatures, there was a marked increase of pressure on explosion (even a doubling of pressure). At lower oxygen contents and lower temperatures the pressure change was smaller.

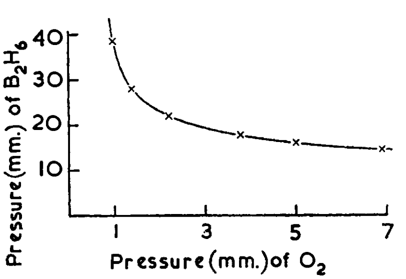


FIG. 15. Partial pressure at "low oxygen content" explosion limit at 140°.

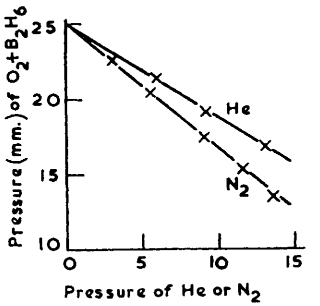


FIG. 16. Effect of nitrogen and helium on the "low oxygen content" explosion limit at 140°; mixtures containing 10% of oxygen were used.

The condition of the surface affects the explosion limit. Explosions produce a coating which must consist of boron, partially oxidised material, and perhaps some hydrides. In some cases it was impossible to obtain an explosion in a clean vessel and it was necessary to induce several with a Tesla discharge before measurements could be made. In one case the first explosion occurred at 40 mm. and then, in subsequent runs, consistently at 25 mm. This suggests that the surface deposit has a lower chain-breaking efficiency than clean Pyrex glass (this contrasts with the results for the oxygen-rich mixtures). The effects of the vessel size (Fig. 14) and of inert gases (Fig. 16) suggest that the surface breaking of chains is the controlling factor at the limit.

While it is true that the above results for mixtures containing a small proportion of oxygen resemble those of Whatley and Pease for similar mixtures, it must be remembered that they obtained explosions with 3 : 1 oxygen–diborane mixtures at 145°. We did not obtain explosions for such a mixture below about 157°. Their procedure must therefore favour, in some way, the achievement of explosive conditions. Perhaps the mode of introduction of the gases and also the long delay allowed by Whatley and Pease were the cause of this.

DISCUSSION

The first and second limits measured by us for 3 : 1 oxygen–diborane mixtures are compared with the results of Roth and Bauer and of Price in Fig. 1. The main difference is that we find the first limits at much lower pressures than they do. This might be a consequence of differences in the purity of the diborane. Price states that his diborane was 99% pure before final fractionation but did not state what impurities might have been present in the sample used. Roth and Bauer could not detect higher hydrides in their sample by infrared analysis. The diborane used by Whatley and Pease was estimated by hydrolysis to be 98% pure. Mass-spectrometric analysis showed that the samples of diborane finally used by us were at least 99·8% pure, though earlier samples had contained ethyl fluoride. On the other hand, the percentage difference between the various second-limit results is not so great, and it should be stressed that, at this limit, all the published results as well as those we have obtained show the opposing effects of diborane and oxygen. It appears to us that Price's pumping procedure was probably inadequate, as pointed out by Roth and Bauer. This and other procedural differences may explain the variability at this limit. At both limits some effect of vessel size was observed, in contrast to the findings by Roth and Bauer and by Price. This may be because we made a bigger variation in the surface : volume ratio. A comparison of our results with those of Whatley and Pease has been reported above.

The general behaviour of the first limit indicates that the breaking reaction in this region is the removal of an oxidising species at the walls (see above). At the second limit there is still some wall effect, indicating that wall-removal of radicals is still an important factor. This is not surprising, because the pressures are low. The effects of inert gases show the occurrence of a breaking reaction in which an inert molecule participates (cf. Price). The way in which an increase in the diborane pressure favours explosion shows that diborane must promote branching. Oxygen, on the other hand, behaves like an inert gas; this again is consistent with the hypothesis that the species involved in the competitive reactions controlling the degree of branching is an oxidising one because then it might be expected to react with diborane, to produce chain branching, but not with oxygen. The inhibiting effect of ethyl fluoride and other hydrogen-containing organic substances is also consistent with this general hypothesis.

A scheme similar to that proposed by Price and shown in Fig. 17 has the required form. According to this, chain breaking occurs by the removal of the active oxidising intermediate X_0 at the wall or by collision of X_0 with oxygen or inert molecules in the gas phase; chain branching occurs either spontaneously or by collision of X_0 with diborane. This leads to the following expression for the limit (in the absence of an inert gas):

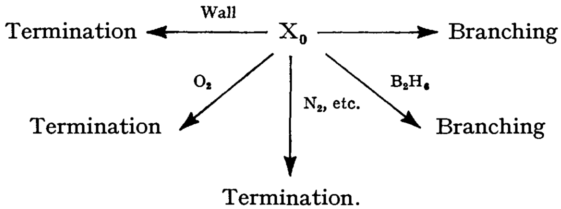


FIG. 17. Reaction scheme.

$$k' + a'p_{B_2H_6} = p_{O_2} + b'/(p_{O_2} + zp_{B_2H_6}). \qquad (A)$$

This is very similar to Price's expression except that he did not include wall-removal. If all the gas-phase processes in Fig. 17 also involve oxygen, having orders one greater than those for the scheme in Fig. 17, the corresponding expression is:

$$k' + a'p_{B_2H_6} = p_{O_2} + b'/[p_{O_2}(p_{O_2} + zp_{B_2H_6})]. \qquad (B)$$

In these expressions, the constants k', a', b', z, etc., may depend on temperature. The constant a' may be a composite one if diborane has an inert-molecule breaking effect in addition to its participation in a branching reaction. Both the above expressions will account for the first and second oxygen pressure limits; and both lead to the conclusion that for variations in the diborane pressure there is only a first limit (*i.e.*, one achieved by a pressure increase). It is necessary to see which accounts for the results more satisfactorily.

A quantitative examination of expressions (A) and (B) was first carried out for 180°, z being taken as unity. The other constants were then fixed from two second-limit points at $p_{O_2} = 12$ and 14 mm., and one first-limit point at $p_{O_2} = 2{\cdot}4$ mm. The results shown in Fig. 18 demonstrate that, for both expressions, but particularly for (B), the effect of oxygen would be expected to be greater than it is found to be. The form of the last term of expression (B) makes this more understandable. This result, therefore, indicates that expression (A) is preferable. The effect of oxygen on the first limit can be reduced by increasing z. Since it is also expected *a priori* that z would be greater than unity, because the diborane molecule is bigger than that of oxygen, calculations of a similar kind were made for $z = 2$. This number is chosen very roughly in order to examine the effect of increasing z; it is not possible to deduce theoretically an accurate value for z because the active species is unknown and molecular diameters are uncertain. A fairly satisfactory reproduction of the first- and second-limit results is then achieved. Similar curves for 170° and 190° obtained by using expression (A) with $z = 2$ are shown in Fig. 19. This Figure also shows the effect of increasing b' by a factor of 1·33 in order to take account of decreasing the vessel diameter (2-cm. vessel). This number was chosen to be proportional to the change in the surface : volume ratio. It will be seen that it accounts for the observed changes in the second limits. It also explains the changes in the first limit (see Fig. 19). These results do emphasise that the reaction scheme of Fig. 17, which is essentially that of Price, does account for the observed limits for mixtures containing an excess of oxygen. It does not account for the limits of mixtures containing only a little oxygen. Equation (A) would lead to the result that, as the oxygen pressure is reduced towards zero, the limiting pressure of diborane would approach about 1·5 mm. at 180°.

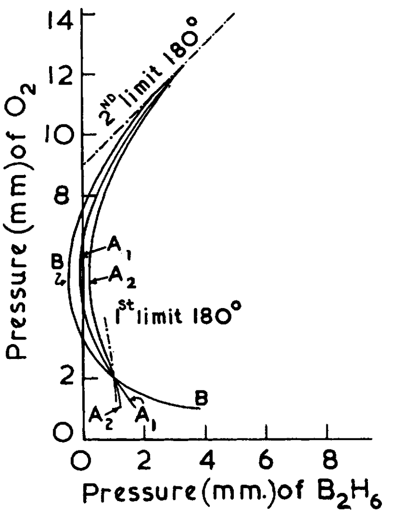


FIG. 18. Calculated graphs for the explosion limits at 180° for scheme A with $z = 1$ (curve A1) and $z = 2$ (curve A2), and for scheme B with $z = 1$, the experimental lines are shown dot-dashed.

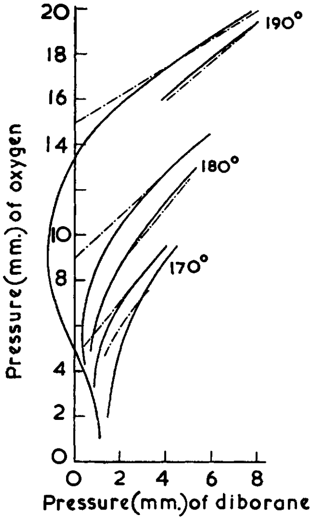


FIG. 19. Calculated graphs of the explosion limits at 170°, 180°, and 190° for scheme A with $z = 2$ showing also the effect of vessel diameter; calculated curves are full lines (in the lower of each pair b′ is increased by a factor of 1·33); experimental ones are dot-dashed, the upper of each pair being for the 4-cm. vessel and the lower for the 2-cm. vessel.

Therefore, as the proportion of oxygen is reduced, the mechanism must change. This is discussed below.

Organic additives exert a chain-breaking effect which is greater than would be expected for a simple inert-molecule effect. To account for this an additional term must be added to the right-hand side of equation (A). For ethyl fluoride it was found that such a term would have to be proportional to the square root of its partial pressure. This cannot be interpreted in any simple manner and implies that when large amounts of ethyl fluoride are added the sequence of reactions is radically changed. The relative effects of the other organic materials are interesting. Suppose a term d_xp_x is added to the right-hand side of equation (A), then d_x can be determined for each additive. It is found that d_x increases with the number of hydrogen atoms in the added molecule (see Fig. 20). If the important species for which branching–breaking occurs is an oxidising radical, then one can readily understand that the activity of such a species would be destroyed or reduced if it abstracted a hydrogen atom from another (*e.g.*, organic) molecule.

By using the constants in expression (A) for the three temperatures for which the data have been analysed, it is found that plotting log k' against $1/T$ gives a straight line (Fig. 21). The slope corresponds to an activation energy of 16·5 kcal./mole; this measures the difference between the activation energies of the spontaneous branching process and the breaking process involving collision with an oxygen molecule.

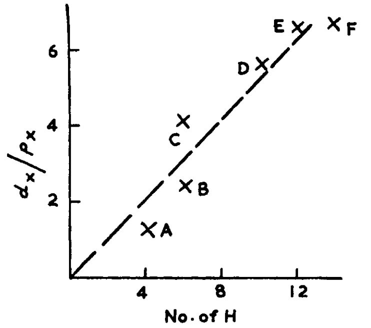


FIG. 20. Depression of the second limit by organic additives as a function of the number of hydrogen atoms in the molecule.

A, CH_4; B, C_6H_6; C, acetone; D, ether; E, cyclohexane; F, n-hexane.

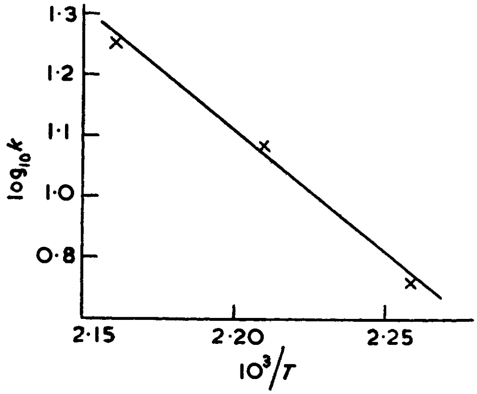


FIG. 21. Temperature-dependence of the spontaneous branching term relative to the breaking term shown as an Arrhenius graph.

The constant a' in equation (A) represents the difference between the branching and breaking effect of diborane. If, very arbitarily, a coefficient of 1·3 is allowed for the breaking effect (relative to oxygen) and then log (a' + 1·3) is plotted against $1/T$ it is found that the slope of the line indicates that the activation energy of the diborane branching process is a little less (3·75 kcal./mole) than that of the oxygen-breaking reaction. This implies (i) that the diborane branching process has a very small energy of activation, and (ii) that the oxygen breaking reaction has an energy of activation not smaller than 3·75 kcal./mole. The variation of b' in equation (A) with temperature indicates that the surface removal process has an activation energy which is approximately the same as, though perhaps a little greater than, that of the spontaneous branching process. This is necessary to account for the small effect of temperature on the first limit, because under our conditions equation (A) indicates that spontaneous branching is considerably more important than diborane branching. From the variation of the effect of organic additives with temperature it appears that the energy of activation of the breaking process which involves these is greater than that of the spontaneous branching reaction.

Any attempt to formulate a precise reaction scheme must, at this stage, involve considerable uncertainty. However, it seems to us that there is some likelihood that the oxidising species (referred to as X_0 in Fig. 17) is the peroxide BH_3O_2. It is known that borine (BH_3) is formed from diborane (B_2H_6) by dissociation and that it has a limited stability. It would be expected that any reaction which caused directly the dissociation of oxygen would have such a large activation energy that it would be unimportant under the present conditions. However, the association of borine with oxygen to give a peroxide BH_3O_2 is not unlikely, and such a species would be expected to have the properties required of X_0. It might isomerise readily to $BH_2{\cdot}O{\cdot}OH$. Spontaneous branching might occur by the disintegration of BH_3O_2 to BH_3O and O, or of $BH_2{\cdot}O{\cdot}OH$ to BH_2O and OH. On the other hand, collision with an inert molecule might allow rearrangement to H_2O and $HB{=}O$ and the latter, for which a satisfactory electronic formula can be written, would be expected to have sufficient stability to reach the wall and be removed. Branching by collision with diborane can be readily explained by processes such as $BH_3O_2 + B_2H_6 \longrightarrow 2BH_3O + BH_3$, though others could be formulated. It is also possible that a species, such as $BH_3{\cdot}O{\cdot}O{\cdot}BH_3$ might be formed and then dissociate into equal halves. If processes of the above type are correct, then the low-temperature oxidation of diborane has some resemblance to the low-temperature oxidation of hydrocarbons in that both involve peroxide intermediates. That this resemblance may in fact be genuine is supported by the observation that changing diborane and oxygen pressures have opposite effects on the reaction rate (see above). Similar effects have been observed in certain cases in the oxidation of hydrocarbons, and the hydrocarbon pressure always accelerates the rate much more than oxygen does.[8]

It has already been concluded that the explosions of mixtures containing little oxygen occur by a different mechanism. In this range, oxygen has a bigger effect than diborane. If the process depended on a preliminary pyrolysis of diborane to an active substance which was attacked by oxygen it would be expected that diborane would have a bigger effect, since pyrolysis has an order of $1\frac{1}{2}$. Therefore it seems that the controlling reaction must be an oxidation.

It has been found empirically that, at the limit, $xp_{B_2H_6}p_{O_2}$ is constant, where x is the yield factor of pentaborane (from Fig. 13) for the mixture (see Table 2). Since B_5H_9 is supposed to be produced *via* BH_3, this may provide a measure of the free BH_3.

TABLE 2.

Added O_2 (%)	3·3	5	10	20	30
$xp_{B_2H_6}p_{O_2}$	6·3	6·5	8·0	7·5	6·3

The effect of added nitrogen would be expected to be:[9]

$$xp_{O_2}\sqrt{(p_{B_2H_6})}[1 + p_{N_2}/(p_{O_2} + p_{B_2H_6})] = k'',$$

if it is supposed that all components interfere with diffusion equally. For the results represented graphically in Fig. 16 (for which x will be constant) the calculated values of k''/x are those shown in Table 3.

TABLE 3.

Added N_2 (as percentage of B_2H_6–O_2)	0	12·5	25	50	75	100
k''/x	11·8	11·8	11·4	10·4	9·7	9·7

The constancy of k''/x is satisfactory and could be improved by assigning to nitrogen a different diffusion coefficient from that of the reacting mixture.

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[8] B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions," Academic Press Inc., New York, 1951, Chap. IV.

[9] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, 3rd edn., 1933, p. 263.

It seems, therefore, that for mixtures poor in oxygen the development of branching depends on the borine (BH_3) and oxygen molecules (cf. the phosphine–oxygen reaction [10]) and that this is competing with chain breaking at the walls. If the present tentative hypotheses are true it appears that, in oxygen-rich mixtures, oxygen reacts so rapidly with borine to form BH_3O_2 that the diffusion to the walls is unimportant and control of the branching below the first limit is by the removal of BH_3O_2 at the walls. In oxygen-poor mixtures, however, the removal of borine by oxygen is slower and so the diffusion of borine to the walls becomes important.

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[10] Dalton and Hinshelwood, *Proc. Roy. Soc.*, 1929, *A*, **125**, 294.