molecule ion from vinylacetylene, the appearance potential observed corresponds to a diacetylene ionization potential of about 10.9 e.v., which tends to corroborate Price and Walsh's value. Thus, we find ourselves in a position of agreeing with Price and Walsh for acetylene and diacetylene but strongly disagreeing for propyne.

It is apparent that we cannot definitely attribute the discrepancy between our work and that of Price and Walsh to any specific cause. However, there is one further observation which must be mentioned. The propyne heat of formation corresponding to Price and Walsh's ionization potential is 304 kcal./mole, and it is of interest that certain molecules decompose under electron impact to give a $C_3H_4^+$ ion with energies quite close to 304 kcal./mole. Thus, it is possible that there is a more or less well-defined state at the energy corresponding to the Price and Walsh ionization potential, but our work would indicate that it is not the ground state. However, such a postulate is not without its flaws, because Price and Walsh observe that the form of the spectrum for propyne is very similar to that for acetylene, for which a value in essential agreement with the electron impact value is obtained. Similarly, good agreement is obtained in the case of diacetylene. It is difficult indeed to understand why the propyne should behave differently from the other two compounds and what the nature of its excited state might be. It would certainly be of interest to have spectroscopic measurements made of the ionization potentials of the substituted acetylenes above propyne.

BAYTOWN, TEXAS

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Observations on Thermal Explosions of Diborane–Oxygen Mixtures[1]

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Diborane–oxygen mixtures explode after an induction period within a range of concentrations at 105° to 165°. Since slow decomposition of diborane is occurring simultaneously at these temperatures, a pyrolysis product—perhaps pentaborane—may be the normal sensitizing agent. Both hydrogen and ethylene narrow the explosion limits.

It has recently been shown[2] that the decomposition of diborane (B_2H_6) takes place slowly in the neighborhood of 100° by a series of quasi-reversible reactions yielding higher boranes and hydrogen. The relation between this process and the reaction of diborane with oxygen is a matter of some interest. Over-all oxidation should be a highly energetic process

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3(s) + 3H_2O(g); \quad \Delta H^0_{298} = -482.9 \text{ kcal.}^3$$

Nevertheless, Stock[4] reports no noticeable reaction with dry air or oxygen (presumably at room temperature), though explosion is said to have followed spillage of liquid diborane when the container was broken.

More recent work by Price[5] indicates that explosion does occur within a range of composition and pressure, though only at temperatures at or above those corresponding to slow decomposition. The latter strongly suggests some interaction with the decomposition process, but no mention is made of anything in the way of an induction period or of an oxygen-sensitized decomposition of diborane. Price determined lower explosion limits by slowly bleeding pre-mixed gases into a clean reaction bulb until explosion occurred. Upper limits were observed by filling the cold reaction bulb to a higher pressure, bringing the thermostated bath up around the bulb, and then slowly evacuating after 1.5 minutes. In some cases, a third limit was also found by increasing the pressure instead of decreasing it as in second limit determinations. Lower limits were located over a range from about 135° to 225° for mixtures containing up to $33^1/_3$% diborane, but no limits could be found for 50% or richer mixtures. Upper limits were located a little above lower limits down to 165°, but at lower temperatures the method gave "upper limits" which actually lay below the "lower limits." There is further mention of an experiment on crossed streams of diborane and oxygen (presumably at one atmosphere), in which spontaneous ignition occurred when the temperature was raised to 132°.

Our interest in the diborane–oxygen interaction evolved from our earlier studies of the decomposition reaction.[2] It had been surmised that oxygen would sensitize diborane decomposition as it is known to do in the case of acetaldehyde, for example.[6] This expectation was based on the assumption that diborane (or the BH_3 radical) being electron-deficient would combine with the virtually unpaired electrons of oxygen to produce a reactive intermediate. No such effect was observed. For

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[2] J. K. Bragg, L. V. McCarty and F. J. Norton, THIS JOURNAL, **73**, 2134 (1951); R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951).

[3] F. D. Rossini, *et al.*, "Selected Tables of Chemical Thermodynamic Properties," Natl. Bur. Standards Circular No. 500 (1952).

[4] A. E. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[5] F. P. Price, THIS JOURNAL, **72**, 5361 (1950).

[6] F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1527 (1935); M. Letort, *J. chim. phys.*, **34**, 428 (1937).

example, in one set of experiments, 80 mm. of diborane was heated for 2 hours at 103.6° with quantities of air up to 12 mm. In all cases, the extent of decomposition was normal (about 15% in the 2-hour period). However, with larger amounts of air, an explosion resulted, but only after an induction period which might be of considerable duration. Further experiments on the explosion process followed as will be described. In addition, the effects of hydrogen and of ethylene were studied. Both were indicated to be inhibitors.

Experimental

Explosions were carried out in a Pyrex bulb of about 7 cm. diameter ($S/V = 0.9$ cm.$^{-1}$), which was heated in a thermostated bath of silicone oil. Gases were introduced separately from storage bulbs at pre-set pressures, the connecting stopcock being opened wide to take full advantage of the stirring action of the jet. Ordinarily, the gas in excess was introduced last, but no significant effects of the order of addition were noted. This method was preferred to the use of pre-mixed gases for reasons of safety, since experience had shown that diborane-oxygen mixtures could be destructively explosive.

In determining limits, as many as 100 experiments were carried out at each of three temperatures—120°, 145° and 165° and at pressures not exceeding about 40 mm. of each gas. The occurrence of the induction period was, of course, a complication in fixing limits. This was resolved arbitrarily by choice of a period of 1000 seconds for observation. Mixtures were described as explosive or non-explosive depending on whether a flash was observed in this length of time.[7] Limits so determined were reasonably sharp at 120° to 165°. At lower temperatures the transition was too gradual for good definition, whereas at higher temperatures explosion was likely to be encountered while the second gas was being introduced

The formation of solid deposits is a further complication. In the early work, the reaction bulb was cleaned after each experiment. This procedure was very time-consuming, and was later abandoned when it became apparent that limits were much the same in bulbs which had accumulated a deposit of solid reaction products.

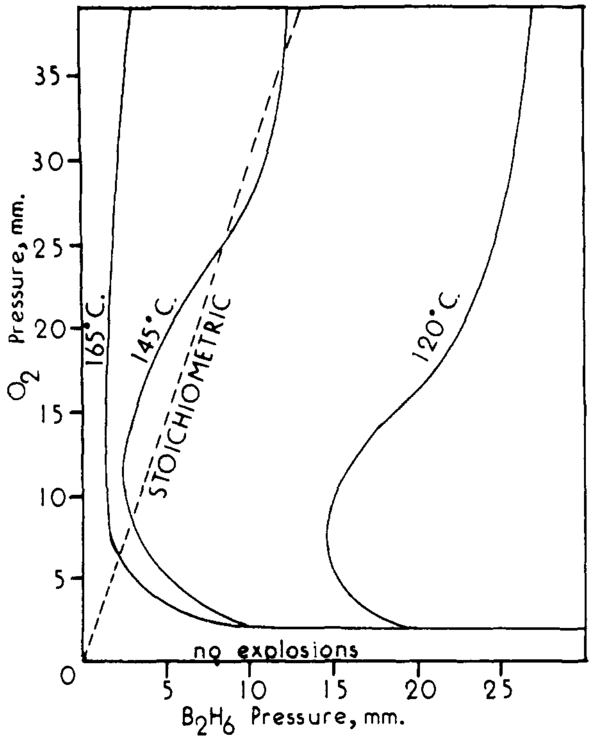

Fig. 1.—Diborane-oxygen explosion limits.

Diborane was prepared in the laboratory and purified by low temperature fractionation. Analysis by hydrolysis indicated a purity of 98% or better. Other gases were obtained from tanks, and were thoroughly dried before use.

Results

The results of the limit determinations at 120°, 145° and 165° are presented in Fig. 1, the curves being constructed from data on induction periods such as appear in Table I. Although successive determinations indicated some variability in the limits, it is believed that the general forms of the curves are authentic. Starting at the lower right-hand corner of Fig. 1, it will be noted that a rich limit is encountered at about 2 mm. of oxygen, and is roughly independent of both diborane pressure and temperature. Each isotherm then starts to ascend at a diborane pressure which is lower the higher the temperature, and even turns to give what amounts to an explosion peninsula. The result is that within a range of diborane pressures there is a lower and an upper limit of oxygen pressure, these limits being narrowed as the temperature is decreased. Only at the intermediate temperature (145°) is there an indication of a true three-limit condition. For the stoichiometric $1B_2H_6$–$3O_2$ mixture (dotted line, Fig. 1), the explosion curve is probably cut three times at total pressures of 11, 33 and 48 mm. It will also be noted that at 120° only rich mixtures were found to be explosive in the pressure range covered.[8]

TABLE I

INDUCTION PERIODS IN DIBORANE-OXYGEN EXPLOSIONS

B_2H_6, mm.	O_2, mm.	Ind. period, sec.
	120°	
17.3	19.3	>1000
16.9	16.2	157
16.3	8.9	592
16.1	6.6	137
16.5	3.2	3
15.3	2.4	>1000
	145.5°	
8.2	26.3	>1000
8.2	23.8	2
7.7	22.7	9
	Immediate explosion down to	
7.0	3.5	11
9.9	2.5	5
9.9	2.0	16
9.9	1.5	>1000
	165°	
3.2	52.2	>1000
3.6	49.2	3
	Immediate explosion down to	
3.5	3.5	10
2.9	3.4	>1000

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(7) The flash was bright green and often accompanied by an audible "ping" at higher oxygen concentrations (fuel-lean mixtures). At lower oxygen concentrations the flash was reddish and less easy to detect.

(8) Explosive ranges found at 103° lay even further to the right of Fig. 1 Variability in the induction period precluded mapping of the data

Our lower limits for the stoichiometric mixture at 145° and 165° (11 and 9 mm., respectively) are in general agreement with those of Price[5] (16 and 15 mm., his Fig. 1), but there the similarity ends. His "second limit" at 145° would lie below the first limit, whereas ours is definitely above; and at 165° our second limit (if it exists) would lie at far higher pressures. Further, we readily located limits for mixtures richer than 50% diborane, which Price describes as non-explosive. We would agree, however, that stoichiometric mixtures are non-explosive at 120° and below, within the 1000-second induction period and over the pressure range covered.

The existence of a second limit naturally suggests chain termination in the gas phase by a three-body collision. The expected inert-gas effect on the second limit has been reported by Price[5] in experiments with nitrogen and hydrogen at 180°, with the implication that direct reaction between diborane and oxygen is somehow involved in the explosion process. However, the induction periods encountered at the lower temperatures of our experiments indicate that the situation is somewhat more complex. It has already been mentioned that diborane is actively pyrolyzing at these temperatures, and that the rate seems to be unaffected by small amounts of oxygen (as air). We are therefore inclined to assume that a pyrolysis product, rather than diborane itself, is responsible for the onset of explosion. Such a product might be pentaborane, since Price has shown that this substance reacts explosively with oxygen at low concentrations even at room temperature.[9] Unfortunately, we were not able to obtain a sample of pure pentaborane in order to test this supposition.

Additional information of a qualitative nature bearing on this question was obtained from observations on the effect of hydrogen on the explosion limits. The experiments were originally undertaken to determine whether diborane would sensitize hydrogen–oxygen mixtures at low temperatures. When no immediate results were obtained, emphasis was shifted to the effect of hydrogen on diborane–oxygen explosion limits. Some grounds existed for expecting such an effect if pyrolysis is a necessary preliminary, since Clarke[2] had found that hydrogen (a reaction product) partially suppresses the reaction. An effect on explosion limits was in fact observed. For example in the absence of hydrogen with 12 mm. of diborane at 145°, explosions occurred between 1.4 and 28 mm. of oxygen within the 1000-second observation period. With 25 mm. of hydrogen present, limits were narrowed at 2.9 and 15 mm. of oxygen. Since no inert-gas effect was found when helium was substituted for hydrogen (the limits were unchanged), it is believed that this result further substantiates the view that a pyrolysis product rather than diborane itself is essential to the explosion.

Our final observations concern experiments with ethylene as diluent. It had been shown[10] that boron triethyl–oxygen mixtures are explosive at low pressures and room temperature, and that *n*-butane–oxygen mixtures can be ignited in this way by addition of boron triethyl. It was also known[11] that boron triethyl is formed from diborane and ethylene at 100° and above. It was, therefore, concluded that addition of ethylene to diborane–oxygen mixtures should sensitize the latter. Once again, the reverse was found to be true. Ethylene proved to be an effective inhibitor. For example, with 8 mm. of diborane at 145° explosions were observed between 2.2 and 24 mm. of oxygen. With 25 mm. of ethylene also present, the limits were completely closed up—no explosions whatever occurred. Moreover, this inhibiting effect was maintained down to 2 mm. of ethylene. However, in one experiment at 70° when diborane and excess ethylene were first allowed to react alone for 4 hours, subsequent addition of oxygen resulted in an immediate explosion, presumably due to the formation of boron triethyl in considerable amount.

These results present an interesting puzzle. Failure of the postulated pyrolysis product to function as a sensitizing agent in the presence of ethylene could be attributed to its suppression by ethylene in favor of boron triethyl formation, since both pyrolysis and ethylene addition have been assumed to involve the same B_3H_9 radical as intermediate.[12] But this implies that boron triethyl is being formed, but that the excess of ethylene is preventing boron triethyl–oxygen explosions in some way. Although this remains a possibility, no experimental data are available for confirmation.

Whatever the full explanation of these observations may be, it seems reasonably clear that neither diborane nor the BH_3 radical reacts directly with oxygen under the experimental conditions but that a pyrolysis product is normally involved in the explosion process. Detailed interpretation awaits further investigations.

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[10] R. S. Brokaw, E. J. Badin and R. N. Pease, *ibid.*, **70**, 1921 (1948).

[11] D. T. Hurd, *ibid.*, **70**, 2053 (1948). Also paper in press, A. T. Whatley and R. N. Pease.

[12] R. P. Clarke and R. N. Pease, THIS JOURNAL, **73**, 2132 (1951). Also paper by A. T. Whatley and R. N. Pease, in press.