[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Luminous Reaction of Pentaborane and Oxygen at and Below the First Pressure Limit of Explosion[1]

BY FRASER P. PRICE

The reaction of pentaborane with oxygen at room temperature in spherical Pyrex bulbs has been investigated. Below the first explosion limit a bluish light is emitted the time dependence of which is described by $-\mathrm{d}I/\mathrm{d}t = kI^2$ where I is light intensity and k a constant. This constant increases with increasing pentaborane pressure but decreases with increasing oxygen pressure. The first explosion limit can be expressed by $P_{O_2} \times P_{B_5} - 3.36P_{B_5}/r - 1.92/r = 0$ where the P's represent pressures and r is the radius of the spherical bulb. The types of reaction schemes necessitated by the explosion limit and luminous reaction data are presented and discussed.

When pentaborane and oxygen are mixed at pressures below their first explosion limit at room temperature a luminous reaction occurs and a white solid is deposited on the walls of the vessel. This state of affairs is rare as most potentially explosive systems do not emit light below the first explosion limit, and the reaction rate below this limit is negligibly small.[2] The thermal decomposition of alkyl nitrate vapors at elevated temperatures shows a qualitative similarity to the phenomena described below.[3] The light emitted by the pentaborane–oxygen reaction is bluish in color, is most intense immediately upon mixing and fades out over a period of one to two minutes. This paper describes a preliminary investigation of the effect of reactant pressures on the time rate of disappearance of this light and also the determination of the first explosion limit for this system.

Experimental

Materials.—Pentaborane was prepared in this Laboratory by pyrolysis of diborane and was purified on the day of use by repeating a cycle of freezing in liquid N_2, pumping and thawing three times. Prior to such purification analyses on the mass spectrometer indicated better than 99.5% purity.

Oxygen was obtained from the G. E. Schenectady Works and was used without further purification. The tank pressure was always above 1800 p.s.i. to insure low moisture content.

Apparatus.—A conventional vacuum line was used for the routine gas manipulations. To this line was attached, by means of a flexible copper tubing, the pipet–explosion bulb system illustrated in Fig. 1. The bulb was mounted inside a wooden box blackened on the interior. Also in this box was a Type 935 Phototube so mounted that it would be activated by the light coming from the bulb. In order to increase the response of the phototube, an aluminum mirror was placed behind the reaction bulb. The phototube was connected to an amplifier which, in turn, actuated a G. E. Photoelectric Recorder. In this manner a time–intensity trace could be obtained. The linearity of the phototube–amplifier circuit was checked by interposing fogged photographic plates of known relative density between the phototube and a constant light source. The setup was linear to better than 1%.

Since constancy of wall conditions of the bulbs was desired both from an optical and a chemical viewpoint, a number of Pyrex bulbs were made up. These could be interchanged rapidly. They were cleaned after reaction by rinsing with distilled water, filling with concd. C.P. nitric acid, immersing in boiling water for 1 hr. and rinsing 6 times with distilled water. They were subsequently dried by attaching to a manifold and pumping for at least 3 hours at room temperature.

Method.—The procedure after purifying the pentaborane and storing it in a freezeout in liquid nitrogen was as follows. The entire system was pumped down to below 50 μ, stopcock C (see Fig. 1) was closed and B turned so as to close off the volume between it and C. Then B_5H_9 was admitted to the system and the pressure noted. Stopcock A was closed and B and C manipulated to admit the gas in the pipet to the reaction bulb. The volumes of the bulb and pipet were such that about 10/1 advantage in reading the pressure was obtained. Next stopcock C was closed and the system again pumped down. Oxygen was then admitted only to the pipet, the volume between stopcocks B & C being kept evacuated. After noting the pressure, stopcocks A and B were manipulated so that mercury from the reservoir could compress the oxygen up into the tube below stopcock C. The mercury was leveled so that the oxygen pressure was one atmosphere. Stopcock C was opened and the course of the reaction followed by the phototube. The volume occupied by the oxygen immediately prior to its admission to the reaction bulb was so small compared to that of the bulb that no correction needed to be applied. In effect all the oxygen went into the reaction bulb immediately. If the pressures of the reactants were such that the first limit had been exceeded, only a bright flash occurred. This appeared as a needle-like trace on the time–intensity record which had neither a build up nor a tail off. On the other hand, if the pressure was below the limit a trace was obtained which reached maximum intensity immediately and fell off slowly with time over the period of about a minute or two.

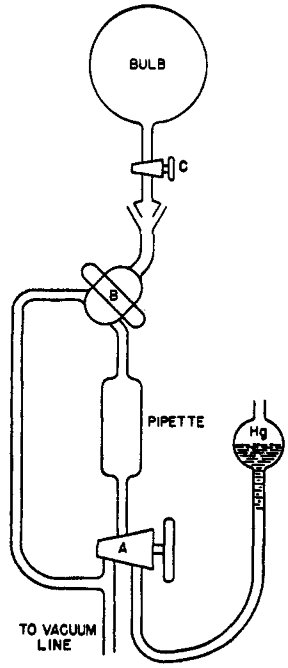

Fig. 1.—Gas pipet and reaction bulb.

In the work described below, in order to get comparable results and not to influence the observed light intensity by increased coating of the vessel walls, all the experiments described were performed after one reaction with 1 mm. B_5H_9 and 1 mm. O_2 had been run in the bulb.

The procedure involved in determination of the explosion limit was the same as that outlined above except that the pressures of reactants used were close to the critical ones.

Results

First Explosion Limit.—If pentaborane and oxygen are mixed above a certain critical pressure, explosion results. This is evidenced by a bright flash of light, but as the pressures required are only of the order of a few millimeters of mercury, the apparatus is never broken. The effect of

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(1) This work done under contract with U. S. Army Ordnance.

(2) R. H. Dalton and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A125**, 294 (1929); P. Gray and H. Melville, *Trans. Faraday Soc.*, **31**, 452 (1935); G. Von Elbe and B. Lewis, *J. Chem. Phys.*, **7**, 710 (1939).

(3) P. Gray and A. D. Yoffe, *Proc, Roy. Soc.* (*London*), **A200**, 114 (1949),

TABLE I

EFFECT OF BULB SIZE AND COATING ON FIRST EXPLOSION LIMIT OF B_5H_9 O_2-MIXTURES IN SPHERICAL PYREX BULBS AT ROOM TEMPERATURE

Bulb radius, cm.	1.85							3.31							
$P_{B_6H_6}$, mm.	0.77	0.83	4.45	4.36	1.00	1.74	1.57	1.03	1.01	1.98	1.94	2.98	3.01	4.02	4.08
P_{O_2}, mm.	2.9	2.8	1.9	2.1	2.7	2.2	2.4	1.5	1.66	1.32	1.33	1.18	1.25	1.13	1.19
Explodes	Yes	No	No	Yes	No	No	No	No	Yes	No	Yes	No	Yes	No	Yes

Bulb radius, cm.	3.31[a]						4.95					
$P_{B_5H_5}$, mm.	0.98	1.01	3.82	3.68	1.99	1.99	1.04	1.04	2.06	2.02	5.1	4.9
P_{O_2}, mm.	1.69	1.58	1.21	1.23	1.33	1.45	1.13	1.07	0.96	0.89	0.80	0.86
Explodes	Yes	No	No	Yes	No	Yes	Yes	No	Yes	No	No	Yes

[a] Bulb coated with paraffin.

vessel size and wall coating on the first explosion limit are given in Table I.

The figures in Table I define the boundary between the non-explosive and explosive regions of the composition diagram. If plots of P_{O_2} *vs.* $1/P_{B_5}$ are made, straight lines result.

Thus a relationship of the following type must hold at the limit

$$P_{O_2} = a/P_{B_5} + b \qquad (1)$$

Values of the constants a and b are given in Table II.

TABLE II

VALUES OF a AND b OF EQUATION 1, FOR DIFFERENT RADIUS BULBS

Radius, cm.	a	b
1.85	0.909	1.80
3.31	.643	1.00
4.95	.370	0.74

These figures show that both a and b depend on the radius of the bulb and furthermore the best dependence that can be found is that they both are proportional to the reciprocal of the radius. All the data in Tables I and II can be combined and rearranged into the equation for the first explosion limit

$$P_{B_5} \times P_{O_2} - \frac{3.36 P_{B_5}}{r} - \frac{1.92}{r} = 0 \qquad (2)$$

where r = radius of bulb in cm.

The conclusions that can be drawn from these data are presented below in the section on discussion.

Luminous Reaction.—All work on the time dependence of luminosity was done at room temperature in Pyrex bulbs 3.3 cm. in radius coated with reaction products. The time-intensity traces were analyzed and it was found that the reciprocal of the intensity when plotted against time yielded a straight line.

TABLE III

SAMPLE RUN

B_5H_9 = 2.95 mm.; O_2 = 0.696 mm.; room temp.

Time (sec.)	I	$(1/I) \times 10^2$	$k \times 10^2$ (intensity × sec.)$^{-1}$
0	33.4	2.99	
1	28.7	3.48	0.49
2	21.3	4.69	1.21
3	16.7	5.98	1.29
4	13.9	7.19	1.21
5	12.0	8.33	1.14
		Av.	1.21

This implies a relationship of

$$-\mathrm{d}I/\mathrm{d}t = kI^2 \qquad (3)$$

where I = light intensity in some relative units.

The results of a typical run are given in Table III. The low first value of the slope "k" in Table III is probably due to a low value of the intensity at zero time resulting from the inability of the recorder to follow the phototube current rapidly enough.

A summary of the results obtained with varying pentaborane and oxygen is given in Table IV. The last column in this table gives the extrapolated values of the light intensity at zero time.

TABLE IV

SLOPES OF TIME *versus* RECIPROCAL INTENSITY PLOTS FOR PENTABORANE-OXYGEN REACTION

Run	Init. $P_{B_5H_9}$, mm.	Init. P_{O_2}, mm.	$k \times 10^2$ (intensity × sec.)$^{-1}$	I_0
126D	1.03	1.46	0.105	715
J	1.01	1.23	.138	312
C	1.02	1.06	.105	208
I	1.02	0.84	.157	76
G	0.99	.74	.408	61
128J	1.98	1.17	.443	400
B	1.98	1.09	.445	286
D	2.02	0.89	.616	104
F	1.98	.68	.624	51
H	1.99	.39	1.58	20
129L	2.98	1.18	0.835	1000
B	2.98	1.03	.833	400
D	2.96	0.87	.941	77
F	2.93	.70	1.20	45
H	2.99	.35	2.26	9
130B	4.02	1.13	0.931	167
D	4.07	0.89	1.24	74
F	4.01	.71	1.25	35
H	4.05	.37	3.60	9

The results summarized above show that the slope, k, increases with both decreasing initial oxygen pressure and increasing pentaborane pressure. The effects are very roughly linear in both oxygen and pentaborane. The initial light intensity varies little with the initial pentaborane pressure and roughly exponentially with the initial oxygen pressure.

The effect of diluting the mixture with nitrogen was next investigated. Unfortunately, the phototube amplifier had changed its calibration so that direct comparisons with the experiments cited above cannot be made. However, the results presented below show that the presence of nitrogen has very little effect on the rate of disappearance of luminescence. No corresponding experiments on the effect of adding nitrogen on the explosion limit were made.

TABLE V

EFFECT OF NITROGEN ON RATE OF DISAPPEARANCE OF LUMINESCENCE IN $B_5H_9 + O_2$ REACTION

3.31 cm. bulb; room temp.

Run	P_{B_5}, mm.	P_{O_2}, mm.	P_{N_2}, mm.	k (intensity × sec.)$^{-1}$
118H	1.03	0.98	0.0	0.195
E	1.00	.99	1.15	.185
C	1.01	.98	2.43	.204
D	1.02	.98	3.70	.204
F	1.01	.99	4.97	.234
G	1.03	.97	6.25	.228

Discussion

In the following discussion it will be assumed that the reactions are of the branched chain type. This is indicated by the fact that there is an explosion limit. At the limit the rate of chain branching reactions must equal that of the chain breaking reactions. Equation (2) describes this state of affairs more quantitatively. This type of expression results from the solution of the steady state equations for chain carriers in some reaction mechanism and appears in the denominator of the rate expression. It is most probable that the first term of equation (2) represents chain branching and the last two the breaking processes. Since termolecular branching would be extremely unlikely, the order of the first term must be the result of a rapid reversible equilibrium followed by a slower branching step. The chain breaking reactions depend on the geometry of the vessel and therefore must involve destruction of chain carriers at the wall. Also, since the dependence is on the reciprocal of the first power of the radius the chain breaking efficiency of the wall must be very low.[4] This is known to be so for the $H_2 + O_2$ reaction in Pyrex vessels.[5] In this case, however, even paraffin must have about the same chain breaking efficiency as Pyrex as shown by the data in Table I.

From these facts the most probable reaction mechanism seems to be

$$f(O_2, B_5H_9) \longrightarrow X \qquad (4)$$

$$\left.\begin{aligned} X + B_5H_9 &\rightleftarrows Y && (5)\\ Y + O_2 &\longrightarrow \alpha X + \text{products} && (6)\end{aligned}\right\}\ \text{branching}$$

$$\left.\begin{aligned} X &\longrightarrow \text{wall} && (7)\\ Y &\longrightarrow \text{wall} && (8)\end{aligned}\right\}\ \text{breaking}$$

where α is a number greater than one and where X and Y are chain carriers and equation (6) represents the formation of chain carriers by pentaborane, oxygen or both.

When the steady state assumptions are applied to this mechanism they lead to the following

$$X = \frac{f}{k_7 + K_5k_8[B_5] - (\alpha - 1)K_5k_6[O_2] \times [B_5]} \qquad (9)$$

$$Y = \frac{K_5[B_5]f}{k_7 + K_5k_8[B_5] - (\alpha - 1)K_5k_6[O_2][B_5]} \qquad (10)$$

where $K_5 = k_5/k_{-5}$ and it is assumed that $k_{-5}k_{>>6}$ $[O_2] + k_8$. This assumption is probably valid in view of the necessity of keeping a high enough concentration of Y to maintain the equilibrium. By comparing the denominator of the right hand member of equation (9) or (10) with equation (2) it can be seen that

$$\frac{k_7}{(\alpha - 1)K_5k_6} = \frac{1.92}{r} \text{ and } \frac{k_8}{(\alpha - 1)k_6} = \frac{3.36}{r}$$

Now let us consider the data on the light producing reaction.

The stoichiometry of the reaction indicates that the pentaborane is in large excess. Therefore, the exponential dependence of initial light intensity on initial oxygen pressure as well as the relative insensitivity of the initial intensity to the pentaborane pressure might be expected.

The form of equation (3) makes it impossible that the light could come from the decomposition of some active particle formed in large quantities at the start of reaction, for if this were the case the rate of change of the intensity would depend only on the first power of the light intensity. The light intensity can also be regarded as a measure of the number of light emitting acts per unit time and hence can be considered to be a measure of the rate of change of some concentration. Since the intensity is large at the start and decreases with time, it cannot be a measure of the rate of change of a chain carrier concentration for this is zero. Therefore the light intensity must be a measure of the rate of change of one of the reactants.

The coefficient k in equation (3) increases with increasing pentaborane. This is what would be expected as the rate of chemical reaction and hence the rate of light production goes to infinity at the explosion limit. The effect of increasing oxygen in decreasing k is much more puzzling. Since the rate of light production, dI/dt, must go to infinity at the explosion limit, either k or I or both must be infinite there. The fact that k decreases with increasing oxygen and still there is a limit presents two alternatives which the present data are incapable of resolving. Either (a), the increase of I with increasing oxygen overwhelms the decrease in k and thus allows an infinite rate to be approached, or (b), at low oxygen concentration there is a reaction in which oxygen acts as an inhibitor. In the latter case, however, the reaction in which oxygen acts as a chain brancher eventually must overwhelm the inhibition reaction so that the rate can approach infinity at the explosion limit. Run No. 129L was made very close to the limit and there is an indication that the value of k here has started to increase. In any event the inhibiting effect of the oxygen must persist very close to the limit. Furthermore, the reaction or series of reactions which represents the inhibition of luminescence must have a less than first order dependence on oxygen. Otherwise there would be no minimum in the values of k.

The form of equation (3) can be explained either on the result of light being emitted from some oxidative step such as that in equation (6) and some of it being reabsorbed in the initiating step 4, or as the result of the light being both absorbed and

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[4] B. Lewis and G. Von Elbe, "Combustion, Flames and Explosions in Gases," Cambridge University Press, 1938, p. 23 ff.

[5] B. Lewis and G. Von Elbe, *J. Chem. Phys.*, **10**, 366 (1942).

emitted from one reaction such as step 5. In the former case, a little absorbed light in the initiating step will introduce a few carriers which upon entering the branched chain will have relatively enormous effects. The fact that boron hydrides decompose when exposed to ultraviolet light is in favor of such a postulate. However, a few experiments made in a spherical quartz bulb under irradiation from a mercury arc failed to produce any marked effect on the rate of disappearance of luminescence. Also pentaborane shows no marked absorption of light in the ultraviolet. The light observed in this reaction was in the visible, bluish in color; however, there is no reason to suppose that this is the only wave length emitted. There must be a whole series of rapid oxidative steps subsequent to that indicated in equation (6), each of which may emit its own characteristic wave length. Thus while equation (6) represents the rate-controlling oxidation and hence the rate of production of light it is quite possible that a whole series of frequencies actually is emitted. In the latter case, if the reaction emitting and absorbing light were the reversible equilibrium shown by equation (5), then the time dependence of luminosity has the correct form. Furthermore, in this case, it is unnecessary to assume light absorption in the initiating step, 4. The difficulty encountered here is that the intermediate, Y, would have to be in equilibrium with the light emitted. Also solution of the equations indicates that the explosion limit expression, 2, should depend on the luminosity.

The work presented and discussed in this paper is admittedly far from complete and many points need further investigation before a definite mechanism can be proposed. However, the author believes that the current interest in the boron hydrides warrants presentation of the data as a stimulus to future investigation of this interesting reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BLACKBURN COLLEGE]

Alkyliodosilanes: Ethyl Series and Monododecyl

BY HERBERT H. ANDERSON,* DONALD L. SEATON AND RICHARD P. T. RUDNICKI

This paper describes four alkyliodosilanes: new ethyltriiodosilane, diethyldiiodosilane, triethyliodosilane and new monododecyltriiodosilane. Triethyliodosilane is prepared through a Grignard reaction, while the other three are made from the appropriate alkylchlorosilane and aniline, followed by hydrogen iodide. Phosphorus triiodide and tetraethoxysilane when heated furnish ethyl iodide rather than ethoxyiodosilanes. Even distillation at low pressure does not yield methoxyiodosilanes or ethoxyiodosilanes after treating an alkoxychlorosilane first with aniline and later with hydrogen iodide.

Whitmore and co-authors had already prepared trimethyliodosilane.[1] Moreover, the existence of all three iodofluorosilanes[2] indicated the stability of all three ethyliodosilanes, now confirmed herein.

Preparation of Alkyliodosilanes.—In the Whitmore method[2] trimethylchlorosilane and the phenyl Grignard reagent yield trimethylphenylsilane, which then reacts with iodine to give trimethyliodosilane and iodobenzene. However, the boiling point of 189° for iodobenzene is too close to that of triethyliodosilane, 193°, for use of an analogous reaction between triethylphenylsilane and iodine.

Ethyltriiodosilane, diethyldiiodosilane and dodecyltriiodosilane were prepared by the Ruff[3] method, wherein he converted trichlorosilane ultimately into triiodosilane. Aniline reacted with the halosilane in a benzene solution; after filtering and washing of the precipitated anilinium chloride, anhydrous hydrogen iodide was passed into the resultant benzene solution; anilinium iodide precipitated and the desired iodosilane was left in benzene solution; distillation followed.

Our chief precautions were: the use of 2.30 mols of aniline per mol of chlorine in the original alkylchlorosilane, with occasional agitation and storage for 20 hours; after filtering anilinium chloride, to test a small portion of filtrate with fresh aniline to check completeness of precipitation; a five-hour passage of gaseous hydrogen iodide[4] into the filtrate, using a system provided with ground joints or closely fitting rubber connections, and also provided with three bulbs containing phosphorus pentoxide; protected filtration of the anilinium iodide and a second passage of hydrogen iodide to check completion of precipitation; all distillations, including that of the solvent benzene, in equipment with ground joints; the chief physical measurements on the day of final purification of each compound; distillation finally in the presence of copper powder.

Triethyliodosilane could not be obtained by the Ruff method from the corresponding chloride, nor from triethylphenylsilane and iodine. It was prepared, in two sections, starting with a total of 120 g. of pure diethyldiiodosilane and 0.41 mol of ethylmagnesium iodide, in anhydrous ether. After standing for 12 hours, during which slight warming occurred, two ether layers were found, the lower of which crystallized in an ice-bath, and was magnesium iodide (with some ether). The crude product consisted of 16 ml. of tetraethylsilane and 9 ml. of triethyliodosilane; thereupon, further distillation several times yielded a final center fraction boiling at 191.5–192.5° uncorrected.

Chemical and Physical Properties.—Ethyltriiodosilane hydrolyzes the most rapidly and vigorously; diethyldiiodosilane hydrolyzes rapidly; triethyliodosilane hydrolyzes readily, although less so than the first two, yet much more easily than the corresponding isocyanate, triethylsilicon isocyanate. All three ethylsilicon iodides are colorless, mobile liquids which fume readily in moist air; dodecyltriiodosilane is colorless, but is somewhat more viscous and does not fume so readily. These four iodides may be kept colorless only in a sealed tube bearing some copper powder; even the determinations of density involved more than usual difficulty.[5] Measurements of refractive index in an Abbe refractometer were impossible in air of 70% humidity.

Analyses.—Many investigators have weighed samples of organosilicon halides and then titrated the available acidity; it has been found possible to use self-filling micropipets for the analysis of certain of these compounds *without weighing the samples*.[6] Several precautions are mandatory with the iodides, however; there is a tendency to lose acidity. A very-thin-walled, soft glass tube holding a weighed sample of the alkyliodosilane was placed in the neck

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[1] F. C. Whitmore and others, THIS JOURNAL, **70**, 433 (1948).

[2] H. H. Anderson, *ibid.*, **72**, 3091 (1950).

[3] O. Ruff, *Ber.*, **41**, 3738 (1908).

[4] To prepare anhydrous hydrogen iodide, one should use water and a mixture of phosphorus and iodine in the atomic ratio of one to five—equivalent to a hypothetical phosphorus pentaiodide, rather than our actual ratio of one to three, which could give traces of phosphonium iodide.

[5] H. H. Anderson, *Anal. Chem.*, **20**, 1241 (1948); see Fig. 2.

[6] H. H. Anderson, THIS JOURNAL, **71**, 1801 (1949). See Table II.