

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY]

Wall Effects in the Oxidation of Boron Triethyl Vapor. Ignition of *n*-Butane¹

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In a recent paper on the oxidation of zinc dimethyl vapor at room temperature,² it was shown that the reaction is autocatalytic, becoming explosive if the pressure of zinc dimethyl exceeds 12–15 mm.; and that it will induce the ignition of *n*-butane. Somewhat similar data on boron triethyl vapor are presented here. Particular attention has been given to the effect of solid products and surface treatment on the oxidation.

Experimental

The apparatus was similar to that used for the oxidation studies of zinc dimethyl.² Spherical reaction bulbs with inside diameters of 4.6, 6.6, 7.4, 9.8 and 12.7 cm. were used. Both the reaction bulb and the oxygen storage bulb were maintained at 0°. The tubing between them was 6 mm. i.d. rather than capillary to permit rapid mixing of reacting gases. Pressures were measured on a direct reading manometer and small McLeod gage designed to read pressures over a range of 0.01–15.0 mm.

Reaction bulbs were cleaned by treatment with boiling concentrated nitric acid followed by rinsing with distilled water. Drying was carried out in an oven at 135°. Coatings were applied after this standard cleaning procedure. Boron triethyl vapor was first admitted to the reaction bulb at the desired pressure. The reaction bulb was then closed off by its stopcock. Oxygen was admitted to the reservoir in an amount sufficient to give the desired final pressure when the connecting stopcock was opened and the gases allowed to mix. Experiments were carried out in a darkened room in order to make observation of faint flashes. Flashes occurred immediately on opening the stopcock, without measurable induction period.

Boron triethyl was prepared from the Grignard reagent and boron trichloride etherate. As a final purification step, 125 g. was fractionated in a helium atmosphere through a 20-plate column. A third fraction of 20 g. (b. p. 95.0°) was used for all experiments. Oxygen and *n*-butane (C. p.) were high purity tank gases.

Results and Discussion

Boron triethyl vapor ignites instantly on admission of oxygen at substantially lower pressures than does zinc dimethyl. A series of runs in clean dry bulbs of diameters between 4.6 and 12.7 cm. diameter gave values as low as 0.10 mm. of boron triethyl in a 5 volume % mixture with oxygen (stoichiometric mixture for combustion to boron trioxide, carbon dioxide and water; 8.70 vol. %). Data are presented in Table I and Fig. 1.

The product of pressure and bulb diameter was found to be approximately constant, as would be expected if reaction chains start in the gas phase and end on the wall.³

(1) The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coordinated by the Applied Physics Laboratory, The Johns Hopkins University. Acknowledgment is also due Dean H. S. Taylor, who has general supervision of this project.

(2) E. J. Badin, D. R. Walters and R. N. Pease, *THIS JOURNAL*, **69**, 2588 (1947).

(3) Cf. C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, 1940, p. 15. Similar results have been obtained for, e. g., the phosphine-oxygen reaction, Dalton and Hinshelwood, *Proc. Roy. Soc. (London)*, **125A**, 294 (1929).

TABLE I
MINIMUM IGNITION LIMITS FOR 5 VOLUME % BORON TRIETHYL IN OXYGEN, TEMPERATURE, 0°.

Bulb diameter, <i>d</i> , cm.	Limit pressure, <i>p</i> , mm.	Partial pressure B(C ₂ H ₅) ₃ , mm.	<i>p</i> × <i>d</i>
Clean dry bulbs			
4.6	7.5	0.38	34
6.6	4.3	.22	28
7.4	4.1	.21	30
9.8	3.1	.16	30
12.7	2.1	.11	27
Bulbs self-coated with products			
4.6	10.7	0.54	49
6.6	9.0	.45	59
7.4	7.3	.37	54
9.8	4.7	.24	46
12.7	3.6	.18	46

A coating of reaction products demands a higher limiting pressure (Table I and Fig. 1), indicating that the solid products are somewhat more effective than the clean Pyrex surface in breaking chains before branching (and ignition)

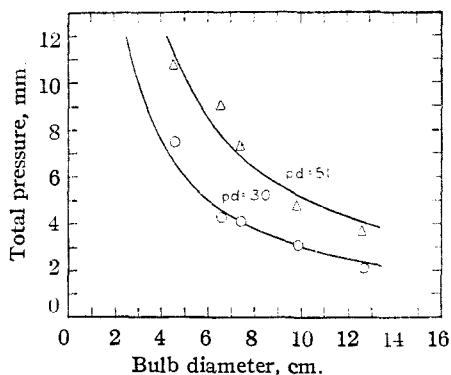


Fig. 1.—Variation of explosion limit with bulb diameter for the oxidation of boron triethyl: Δ , surface self-coated with reaction products; \circ , clean "dry" Pyrex surface.

occurs. This would seem to suggest that other surface coatings might likewise be better chain-breakers than Pyrex. It was therefore somewhat puzzling to find that washing out the clean reaction bulb with solutions of boric acid, potassium hydroxide, potassium chloride, hydrochloric acid or paraffin (1% in pentane) gave substantially the same lower limit as clean Pyrex (4.1–5.1 mm. in 6.5 cm. bulb).

No real evidence was obtained of an upper pressure limit such as might be expected of a branched-chain explosion. However, it was observed that the bright green flash due to ignition was somewhat less intense at higher pressures

(~100 mm.), especially with rich mixtures, though this probably only represents more effective quenching of chemi-luminescence. It was also noted that the radiation emitted by mixtures just above the lower limit was more bluish and much less intense. This recalls Frankland's observation⁴ that a slow current of boron triethyl (or trimethyl) vapor issuing into air burned with a faint blue flame—"the temperature of which is so low that a finger may be held in it for some time without much inconvenience." Evidently, cool flame phenomena are involved near the limit. It was interesting to find that with the coated reaction bulb this cool flame was no longer observed. The bright green flash was observed right down to the limit which, as already stated, was correspondingly higher.

We have no evidence to present regarding the reaction below the low pressure limit, except that there was no pressure-change or detectable deposit in 1,000 seconds. Experiments of Bamford and Newitt⁵ on the oxidation of boron trimethyl and tri-*n*-propyl, by slowly admitting oxygen to the vapor at about 1 mm., indicate a very rapid absorption up to the equivalent of $R_3B:O_2$, with no separation of a condensed product. According to Frankland,^{4,6} the slow admission of oxygen or air to liquid boron triethyl produces ethane-boronic diethyl ester, $C_2H_5B(OC_2H_5)_2$. In any event, there is no evidence of the separation of a solid at these low pressures until the ignition limit is passed.

(4) E. Frankland, *J. Chem. Soc.*, **15**, 363 (1862).

(5) C. H. Bamford and D. M. Newitt, *ibid.*, 695 (1946).

(6) See also Krause, *et al.*, *Ber.*, **61**, 271 (1928); **63**, 934 (1930); a similar observation on boron tri-*n*-butyl by Johnson and Van Campen, *THIS JOURNAL*, **60**, 121 (1938).

This is in contrast to the oxidation of zinc dimethyl vapor where a white mist begins to form immediately on mixing with oxygen.

Finally, a few experiments on the induced ignition of *n*-butane by means of boron tri-ethyl have been carried out, by admitting a stoichiometric mixture of oxygen and *n*-butane (13.3 vol. %) to a bulb containing boron triethyl vapor, the total pressure being 100 mm. With 1 mm. of boron triethyl there was no reaction, but with 3 mm. of boron triethyl there was a violent explosion which travelled back through 6 mm. i. d. tubing to the reservoir flask. However, with 5 or 10 mm. of boron triethyl there was only a faint flash, which was much weaker than that in absence of *n*-butane, and a negligible pressure change.⁷ There thus appear to be sharp pressure limits to this induced oxidation.

Summary

1. Boron triethyl vapor ignites spontaneously in oxygen at partial pressures below 1 mm. in a Pyrex bulb held at 0°.

2. The product of minimum pressure and bulb diameter is constant, indicating that chains start in the gas phase and end on the wall. When the glass surface is coated with reaction products, the minimum pressure is greater.

3. There is evidence of a cool flame phenomenon.

4. Boron triethyl will ignite a *n*-butane-oxygen mixture within narrow pressure limits.

(7) The 3 mm. mixture produced a large pressure decrease, presumably due to condensation of water vapor formed by the combustion.

PRINCETON, NEW JERSEY RECEIVED OCTOBER 18, 1947

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

Analogs of Pteroylglutamic Acid. I. N¹⁰-Alkylpteroic Acid and Derivatives

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The structure of pteroylglutamic acid¹ has been demonstrated and several methods of synthesis have been described.^{1,2}

This factor of the vitamin B complex is identical with the liver *L. casei* factor³ and apparently is related to a number of other substances⁴ isolated from natural sources. All are necessary for the normal growth and development of certain animals and microorganisms. The question immedi-

(1) (a) Angier, *et al.*, *Science*, **103**, 667 (1946); (b) Mowat, *et al.*, *THIS JOURNAL*, **70**, 14 (1948).

(2) (a) Waller, *et al.*, *ibid.*, **70**, 19 (1948); (b) Hultquist, *et al.*, *ibid.*, **70**, 23 (1948); (c) Angier, *et al.*, *ibid.*, **70**, 25 (1948); (d) Boothe, *et al.*, *ibid.*, **70**, 27 (1948).

(3) Stokstad, Hutchings and SubbaRow, *ibid.*, **70**, 3 (1948).

(4) (a) Hutchings, Stokstad, Bohonos, Sloane and SubbaRow, *ibid.*, **70**, 1 (1948); (b) Snell and Peterson, *J. Bact.*, **39**, 273 (1940); (c) Hutchings, Bohonos and Peterson, *J. Biol. Chem.*, **141**, 521 (1941); (d) Mitchell, Snell and Williams, *THIS JOURNAL*, **63**, 2284 (1941); (e) Pfiffner, *et al.*, *Science*, **97**, 404 (1943).

ately arises as to what the biological effect will be when variations are introduced into the structure of the vitamin by chemical methods of synthesis. There is always the possibility of enhancing the desirable effects of the vitamin, and also of producing new compounds which can be used in treating other syndromes. The use of pteroylglutamic acid antagonists in the treatment of blood dyscrasias, leukemia for example, has been suggested by Franklin, Stokstad, Belt and Jukes.^{5a}

Variations of the structure and study of the relationship between structure and biological activity have already received the attention of workers in the field. Dibromobutyraldehyde has

(5) (a) Franklin, Stokstad, Belt and Jukes, *J. Biol. Chem.*, **169**, 427 (1947); (b) Martin, Tolman and Moss, *Archives of Biochemistry*, **12**, 318 (1947); *Science*, **106**, 168 (1947); (c) Franklin, Stokstad and Jukes, *Proc. Soc. Exptl. Biol. Med.*, **65**, 368 (1947); (d) Welch, Heinle, Sharpe, George and Epstein, *ibid.*, **65**, 364 (1947).