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The Air Oxidation of Trialkylboranes

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A study of the air oxidation of trialkylboranes shows that the first boron-carbon bond oxidizes faster than the second and the second much faster than the third; the presence of water prevents the oxidation of the third bond. Oxidation stops at oxygen absorptions corresponding to 73-100% conversion to borate ester. Alcohol yields from the saponification of the oxidation product can correspond under certain conditions to oxidation of more than two of the three boron-carbon bonds. The nature of the numerous by-products including considerable quantities of hydrocarbons is consistent with a series of free radical reactions based on R· and RO· radicals formed by decomposition of an intermediate alkylperoxyboron compound, $-BO_2R$. Peroxides form and decompose primarily during the oxidation of the second boron-carbon bond, and most of the hydrocarbons form during oxidation of the first and second boron-carbon bonds.

The discovery of the hydroboration of olefins to alkylboranes¹ has provided a new method of preparing such derivatives of olefins as alcohols¹ and paraffins.² Hydroperoxidation usually has been used for the conversion of alkylboranes to alcohols in generally good yields. Air oxidation which is reported to give lower alcohol yields with maximum yields corresponding to those of two of the three alkyl groups oxidized,³ has not been widely used.

Previous work has shown that alkylboronperoxy compounds, $-BO_2R$, are formed during the autoxidation of alkylboranes.⁴ Davies⁴ and Zutty and Welch⁴ have shown that these peroxides have some stability, but that they are readily hydrolyzed or decomposed by amines. The hydrolysis products were identified as alcohol, alkylhydroperoxide and trace amounts of ketone or aldehyde. The formation of the ketone or aldehyde was explained by Davies⁴ as a base-catalyzed heterolytic scission of an alkylperoxyboron compound. The fate of all three alkyl groups and of the boron atom after air oxidation and hydrolysis has not been completely established.

This paper reports a study of the kinetics of the air oxidation of trialkylboranes by means of oxygen absorption data and peroxide and other analyses. The products formed during the oxidation and after saponification were identified as completely as possible.

(1) F. G. A. Stone and W. A. G. Graham, *Chemistry & Industry*, 1181 (1955); H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582, 5694 (1956); H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136, 1137 (1957); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 4106 (1959); M. F. Hawthorne, *ibid.*, **82**, 748 (1960); *J. Org. Chem.*, **23**, 1788 (1958); E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(2) H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959).

(3) E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 127; G. E. Coates, "Organo-Metallic Compounds," Methuen and Co., Ltd., London, 1956, p. 57.

(4) R. C. Petry and F. H. Verhoek, *J. Am. Chem. Soc.*, **78**, 6416 (1956); G. S. Kolesnikov and L. S. Fedorova, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, 906 (1958); J. Furukawa and T. Tsuruta, *J. Polymer Sci.*, **28**, 227 (1958); J. Furukawa, T. Tsuruta, T. Saegusa, T. Fueno, R. Sakata and K. Ito, *ibid.*, **28**, 450 (1958); J. Furukawa and T. Tsuruta, *ibid.*, **40**, 237 (1959); M. H. Abraham and A. G. Davies, *Chemistry & Industry*, 1622 (1957); *J. Chem. Soc.*, 429 (1959); A. G. Davies and D. G. Hare, *ibid.*, 438 (1959); N. L. Zutty and F. J. Welch, *J. Org. Chem.*, **25**, 861 (1960).

Experimental

Purification of Materials.—Pure grade Phillips *n*-heptane was passed through alumina and then refluxed and stored over sodium. Pyridine, reagent grade, was distilled from barium oxide under nitrogen and the center cut used. Tetrahydrofuran, reagent grade, was refluxed with calcium hydride, distilled from lithium aluminum hydride, and stored over sodium wire. Dimethylformamide, reagent grade, was refluxed with calcium hydride and then distilled and the center cut used. All materials were stored under nitrogen.

Matheson dry grade air and Matheson prepurified grade nitrogen were used.

Tri-*n*-butylborane, obtained from the Callery Chemical Co., was distilled through an 18-inch column packed with glass helices at 2.5-3.0 mm. of nitrogen; only a center cut was used, b.p. 73-74°. The forerun, b.p. 69-70.5° at 2.5 mm., was somewhat high in boron content, 6.15%, suggesting the presence of (*n*-butyl)₂BH. The B(*n*-hexyl)₃ also was obtained from the Callery Chemical Co. and analysis showed it to be high in boron content. It was treated, therefore, with hexene-1, Phillips pure grade, and 10 wt. % of anhydrous diethyl ether, based on hexene-1, for 6 hours at gentle reflux under nitrogen. The reaction mixture then was vacuum distilled with the 18-inch glass helices-packed column under nitrogen. A center cut was used, b.p. 130° at 2.1 mm. to 137° at 1.5 mm. The material was still impure as shown by the analyses, which indicate the presence of (*n*-hexyl)₂BH.

Anal. Calcd. for C₁₈H₃₆B: C, 81.18; H, 14.76; B, 4.06. Found: C, 79.95; H, 14.61; B, 4.51.

Oxidation Procedure.—A flask was charged in a nitrogen box with 91 g. (0.050 mole) of B(*n*-butyl)₃ with or without 91.0 g. of *n*-heptane or other solvent, or with 133 g. (0.050 mole) of B(*n*-hexyl)₃ with or without an additional substance added. In all cases where heat was evolved on addition of the solvent, *i.e.*, the oxygen and nitrogen-containing solvents, cooling was used to maintain the temperature of the trialkylborane at 25°. The flask was fitted with a gas inlet tube with a fritted-glass thimble sealed to one end of the tube, and the tube was connected to both nitrogen and air cylinders *via* a rotameter and Drierite and Ascarite tubes. A vertically mounted surge flask was used between the condenser and the flask in oxidations where excessive foaming was encountered, *i.e.*, non-diluent oxidations. A -5 to 0° cold trap was mounted above the condenser. The trap was connected to either two liquid nitrogen-cooled traps or two Dry Ice-isopropyl alcohol cooled traps. From these traps part of the exit gas was passed through a needle valve and a rotameter to an A. O. Beckman oxygen analyzer, model E-2, and the rest was discarded. The gas inlet lines were preflushed with air, and the exit lines were preflushed with nitrogen.

Air was passed into the trialkylborane at a rate of 1 liter/min. Oxygen analyzer readings were taken at 1-2-min. intervals during the absorption of the first 70-80% of the oxygen and then at less frequent intervals. Constant temperatures were maintained during the oxidations by external cooling or heating. A Dry Ice-alcohol cooling bath is necessary during the early part of the oxidation.

TABLE I

EFFECT OF TEMPERATURE AND DILUENT ON THE AMOUNT AND RATE OF OXYGEN ABSORPTION AND ALCOHOL YIELD
An air flow rate of 1 l./min. was used in all experiments. All experiments were carried out with 50 wt. % diluent except those without diluents and those with H₂O (21.7 wt. %) and H₃PO₄ (3.8 wt. %).

Mole % Br ₁	Diluent	Temp., °C.	1/3 ^a	Time, hr., for 2/3 ^a	Finish ^b	% of theor. O ₂ absorption ^c	n-C ₆ H ₁₃ OH yield, mole % Uncor. for total O ₂ absorption	Corrected ^d
35 B(<i>n</i> -C ₄ H ₉) ₃	<i>n</i> -Heptane	75	0.5	2.3	9.5 ^e	95	61.0	64.5
35 B(<i>n</i> -C ₄ H ₉) ₃	<i>n</i> -Heptane	25	.5	1.5	10	87	64.7	74.4
35 B(<i>n</i> -C ₄ H ₉) ₃	<i>n</i> -Heptane	10	.5	1.3	6.5	87	77.0	79.2
35 B(<i>n</i> -C ₄ H ₉) ₃	<i>n</i> -Heptane	0	.5	1.2	5	88	80.5	91.4
35 B(<i>n</i> -C ₄ H ₉) ₃	<i>n</i> -Heptane	-25	.5	1.4	6.5	87	70.6	81.0
100 B(<i>n</i> -C ₄ H ₉) ₃	75	.5	1.3	^f	100	86.3	86.3
100 B(<i>n</i> -C ₆ H ₁₃) ₃	75	.5	1.0	4.6	94	62.9	66.9
30 B(<i>n</i> -C ₄ H ₉) ₃	Pyridine	77	.5	1.9	4.8	73	31.2	42.5
28 B(<i>n</i> -C ₄ H ₉) ₃	THF ^g	60	.5	1.1	8.3	97	47.4	49.0
29 B(<i>n</i> -C ₄ H ₉) ₃	DMF ^h	75	.7	4.0	7.2	78	51.5	66.4
20 B(<i>n</i> -C ₆ H ₁₃) ₃	Water ⁱ	75	.5	2.0	6.0	73	48.0	65.4
89 B(<i>n</i> -C ₆ H ₁₃) ₃	H ₃ PO ₄	75	.5	1.0	4.8	83	56.0	67.7

^a Time for cumulative O₂ absorption to correspond to 1/3 or 1 bond oxidized and 2/3 oxidized for next column. ^b Time necessary for no further O₂ absorption. ^c Total O₂ absorbed at that time when no further O₂ will be absorbed, as % of the theoretical amount of O₂ needed to form B(OR)₃ from BR₁. ^d Corrected for % of theoretical O₂ absorption or alcohol yield based on O₂ absorbed. ^e Using an oxidation reactor with a length/diameter ratio for the liquid of 4.4 instead of the 0.4 ratio used in all the other experiments reduced this time to 5.1 hours. ^f Could not be obtained due to excessive foaming in the reactor toward the end of the oxidation. ^g Enough water to provide an excess beyond saturation of the B(*n*-C₆H₁₃)₃ throughout the oxidation. ^h Tetrahydrofuran. ⁱ Dimethylformamide.

Heating is necessary after 0.4–0.6 equivalent of oxygen has been absorbed in runs carried out above room temperature.

In one instance, samples of the reaction mixture were periodically removed with a nitrogen-flushed hypodermic syringe. Part of these samples were immediately diluted with carbon tetrachloride in a nitrogen box and titrated iodometrically. The other part was sealed under nitrogen for subsequent elemental analysis for carbon, hydrogen and boron.

The Dry Ice or liquid nitrogen traps were periodically weighed and the contents analyzed by gas chromatography and/or mass spectrometry. The liquid nitrogen traps were first warmed to -78° after removal and fresh traps were quickly inserted during removal. Samples of the gas not condensed by Dry Ice traps were analyzed by mass spectrometry.

The oxidation was discontinued when the exit gas had the same oxygen concentration as air according to the oxygen analyzer. A sample of the oxidation reaction product then was titrated for peroxide content.

Saponification Procedure.—The oxidation reaction product was treated with 65 g. of sodium hydroxide in 585 ml. of water added dropwise with stirring at 25–30°. Undiluted oxidation products were diluted with 250 ml. of ether prior to saponification. Stirring was continued at 25° for 1 hour after addition of the sodium hydroxide solution. The aqueous layer was extracted three times with 200-ml. portions of ether and extracts dried with anhydrous magnesium sulfate. The ether was removed by distillation, and the alcohol content of the residue was determined by an esterification procedure.⁵ The residue was analyzed also by gas chromatography.

The aqueous layer from the ether extraction was made acid to congo red with concentrated hydrochloric acid. It was extracted three times with 200-ml. portions of ether and the combined ether extracts dried with anhydrous magnesium sulfate. The ether was removed by distillation; the residue consisted of *n*-butyric or *n*-caproic acids and *n*-butyl- or *n*-hexylboronic acids. The solid boronic acids were separated by chilling and filtration. The various acids were identified by physical constants, melting point, freezing point and refractive index, and also by neutral equivalent or boron analysis.

The amount of carbon dioxide formed was determined by the analysis of the non-condensable exit gas. The amounts of butanes, butenes, butadiene, propylene and propane were determined by the analysis of the condensable gas. Water was present in these materials. The amounts of all other products were obtained by the analyses of the alcoholic

saponification product. Some of the hexane and hexene-1 formed during the oxidation of B(*n*-hexyl)₃ was isolated in the Dry Ice traps. The presence of pyridine-N-oxide and alkylated pyridines (infrared and mass spectrometer) was noted in the oxidation with a pyridine diluent. The existence of C₁₁-hydrocarbons was shown qualitatively by gas chromatography.

Results

Oxygen absorption studies show that enough oxygen is absorbed to account for complete oxidation of trialkylborane to borate ester. The first boron-carbon bond oxidizes somewhat faster than the second bond, whereas the second oxidizes considerably faster than the third (Fig. 1). Excellent agreement is obtained between the first two inflection points in the rate curve and the vertical dotted lines. Essentially all of the oxygen introduced at the very beginning of oxidation is absorbed, but very slow oxygen uptake occurs during most of the oxidation of the third bond. A plot of total oxygen uptake against time gives a smooth curve. Identical curves are obtained in all experiments independent of temperature (-25 to 90°) or the presence of solvent or type of solvent.

There is little effect of oxidation temperature, solvent concentration or type of solvent on the rate of oxygen uptake (Table I). The total amount of oxygen absorbed at the point of no further oxygen uptake corresponds to 73–100% of the theoretical amount for conversion to B(OR)₃. Aluminum alkyls in autoxidation experiments under comparable conditions give much faster rates of oxygen uptake.⁶

The rate of oxygen uptake with tri-*n*-butylborane in pyridine is markedly affected by temperature. A temperature of 70° is needed for an oxidation rate comparable to that obtained with *n*-heptane at the same temperature, and at 25° there is very little oxygen uptake. Davies⁴ has suggested that the initial step in the oxidation is the coordination of an oxygen molecule to the boron of the

(5) J. Mitchell, Jr., *et al.*, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 20–32.

(6) S. B. Mirviss, to be published.

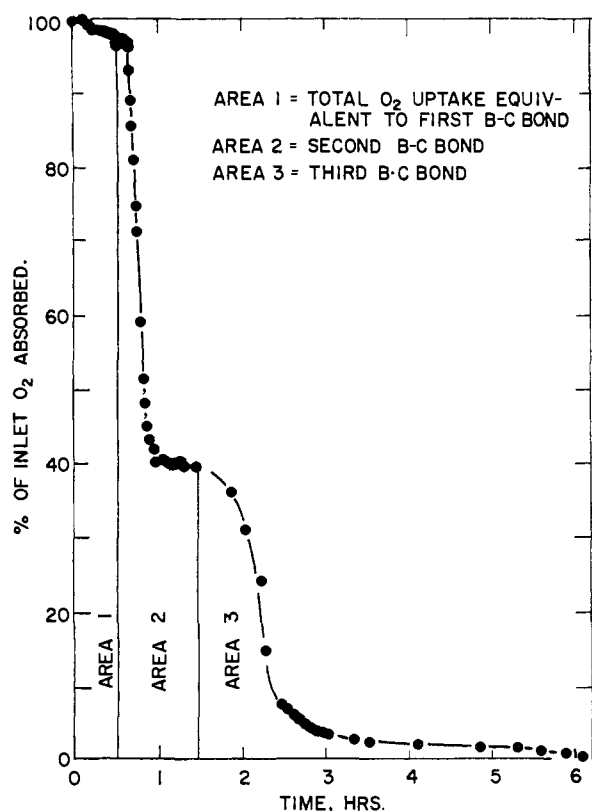


Fig. 1.—Typical instantaneous oxygen absorption rate curve for oxidation of $B(n\text{-C}_4\text{H}_9)_3$ with 50 wt. % (35 mole %) n -heptane diluent at 10° . The vertical lines represent the time at which the total oxygen uptake corresponds to one and two bonds oxidized.

trialkylborane and good evidence for this has been presented by Zutty and Welch.⁷ Thus at lower temperatures competition for coordination with trialkylborane may exist between oxygen and pyridine.

As stated above, the existence of peroxides in trialkylborane oxidation is well documented.⁴ In agreement with the effect of temperature found by Zutty and Welch,⁴ oxidations of a 35 mole % solution of $B(n\text{-butyl})_3$ in n -heptane give higher peroxide content products in oxidations at 0° and -25° than at 10 – 75° . No peroxides were found with pyridine or dimethylformamide as solvents, and very little peroxide was found without solvent. Most of the peroxide appears to form and disappear during the oxidation of the second boron to carbon bond (35–70 mole % oxidized) (Fig. 2).

Saponification of the product of complete oxidation gives the alcohol in yields as high as 86% (Table I). Thus, it is established that more than two boron-carbon bonds in a trialkylborane can be oxidized by air. The low yields with polar solvents compared with the hydrocarbon solvent are unexpected, especially the 31% yield with pyridine. The work of Davies and our work show that peroxides of the trialkylboranes do not form

(7) See ref. 4. Oxygen was passed through dilute boron alkyl solution and then nitrogen was passed in to remove dissolved, unreacted oxygen. Aliquots of the reaction mixture still showed an increase in peroxide content with time despite the removal of dissolved oxygen.

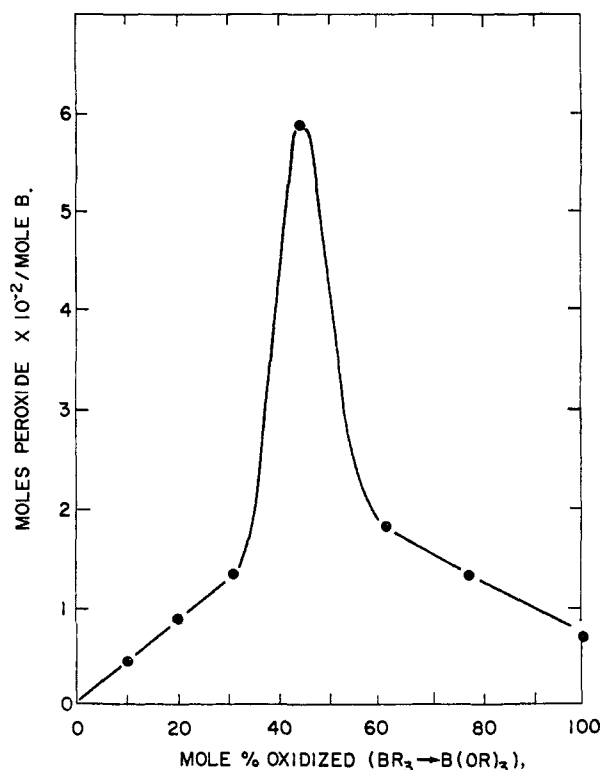


Fig. 2.—Effect of the degree of oxidation on peroxide content; $B(n\text{-butyl})_3$ air oxidation without diluent at 90° .

in pyridine.⁴ Reaction by-products, discussed below, appear to arise from peroxides, and hence a good yield was expected with pyridine. The effect of temperature on alcohol yield is striking with an optimum yield at about 0° . A lower alcohol yield is obtained in $B(n\text{-hexyl})_3$ oxidation than in $B(n\text{-butyl})_3$ oxidation due to the lower purity of the $B(n\text{-hexyl})_3$. The thermal sensitivity of $B(n\text{-hexyl})_3$ results in hydride and olefin formation during purification as noted by Ashby.⁸

The air oxidation of trialkylboranes leads to the formation of olefin and paraffin hydrocarbons. The presence of hydrocarbon by-products never has been noted in previous oxidation studies of trialkylboranes with air, O_2 or H_2O_2 .^{1,4} The yield of butane and butene represents 15–16.5 mole % of the butyl groups in oxidations with $B(n\text{-butyl})_3$ regardless of reaction temperature or diluent. Tetrahydrofuran produces a very high C_4 -hydrocarbon yield of 44 mole %. Most of the hydrocarbons are formed during the oxidation of the first two B-C bonds, which includes the period of greatest peroxide formation and disappearance. The molar ratio of n -butane/1-butene, or n -hexane/1-hexene obtained in experiments with $B(n\text{-hexyl})_3$ is consistently greater than 3/1, and is highest with polar solvents, 10–16/1.

The 1-butene is always contaminated, regardless of temperature, with 6–7% of *cis*-2-butene, 10–25% of *trans*-2-butene and traces of isobutylene. The formation of 2-butene from *sec*-butylboron compounds in the $B(n\text{-butyl})_3$ is precluded by the purity of the latter and the absence of *sec*-butyl alcohol in the product.

(8) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

TABLE II
ELEMENTAL ANALYSES ON PARTIALLY OXIDIZED B(*n*-BUTYL)₃
Undiluted B(*n*-butyl)₃ air oxidation at 90°

Oxidn. time	Mole % oxidized ^a	Analyses, %				Empirical formula	Composition, % =BOH compound ^c
		C	H	B	O ^b		
Original							
B(<i>n</i> -C ₄ H ₉) ₃ ^d	0	79.22	15.04	5.91	...	BC ₁₂ H ₂₇	(A)
15 min.	10	72.47	13.72	5.81	8.00	BC _{11.2} H _{25.6} O _{0.9}	(A) + (B) + 18% (C)
30 min.	21	72.33	13.82	5.84	8.01	BC _{11.1} H _{25.6} O _{0.9}	(A) + (B) + 18% (C)
45 min.	31	69.93	12.99	6.01	11.07	BC _{10.5} H _{23.4} O _{1.3}	(B) + (D) + 39% [(C) + (E)]
1 hr.	45	66.68	12.41	5.90	15.01	BC ₁₀ H _{22.4} O _{1.7}	(B) + (D) + 49% [(C) + (E)]
1.5 hr.	70	60.45	11.11	5.97	22.47	NC _{9.1} H _{20.2} O _{2.3}	(D) + (F) + 73% [(D) + (G)]
2 hr.	78	59.70	11.03	6.37	22.96	BC _{8.5} H _{18.9} O _{2.5}	(D) + (F) + 88% [(E) + (G)]
3 hr. ^e	82	59.68	11.11	6.41	22.80	BC _{8.4} H _{18.8} O _{2.4}	(D) + (F) + 90% [(E) + (G)]

^a Mole % oxidized is based on the total amount of O₂ absorbed for converting B(C₄H₉)₃ to B(OC₄H₉)₃. ^b Based on difference. ^c Based on % C and % H analyses; these compositions are approximate and may not represent all the components present: (A) = (C₄H₉)₃B, (B) = (C₄H₉)₂B(OC₄H₉), (C) = (C₄H₉)₂BOH, (D) = C₄H₉B(OC₄H₉)₂, (E) = C₄H₉B(OC₄H₉)(OH), (F) = B(OC₄H₉)₃, (G) = (C₄H₉O)₂BOH. ^d Calcd. for B(C₄H₉)₃: C, 79.11; H, 14.95; B, 5.94. ^e Oxidation took 9.5 hr. to get 100% of theoretical absorption (see note a); at this point there was no O₂ uptake. Boron analysis on the product at the end was difficult (poor reproducibility) and the composition is approx. BC_{7.7-9.3}H_{15.9-20.3}O_{2.0-2.7}.

Elemental analyses of samples removed periodically during the oxidation of B(*n*-butyl)₃ without solvent show the loss of butyl groups as volatile products from the B(*n*-butyl)₃ during oxidation and the formation of -BOH compounds. These analy-

ses (Table II) show that as oxidation proceeds, the boron and oxygen contents of the liquid reaction mixture increase, but the carbon and hydrogen contents decrease more than expected for oxygen absorption alone. After the absorption of O₂ has reached the equivalent of two boron-carbon bonds oxidized, there is little change in the analyses. This suggests the evolution of most of the C₄-hydrocarbons during the oxygen absorption equivalent to oxidation of the first two boron-carbon bonds. The decrease in carbon content at the point of 82% oxidation corresponds to 30% of the three butyl groups lost. Only 15% of the three butyl groups, however, could be isolated as C₄-hydrocarbons, and thus other by-products may form from the remaining butyl groups lost.

A considerable number of by-products other than C₄-hydrocarbons are formed during the oxidation of B(*n*-butyl)₃ and are listed below. Most of these by-products are found in the products of saponification of the oxidation reaction mixture.

By-product	Mole % on B(<i>n</i> -butyl) ₃ ^d
<i>n</i> -Octane	0.1-8.0
<i>n</i> -Butyraldehyde	0.7-1.7 ^b
Di- <i>n</i> -butyl ether	(0-1.0)
4-Octanone	(0-0.5)
<i>n</i> -Butyl <i>n</i> -butyrate	(0-0.4)
<i>n</i> -Butyric acid	0.3-2.3
<i>n</i> -Butylboronic acid	0.4-4.6 ^c
CO ₂	Traces
Propylene	Traces
Propane	Traces
<i>n</i> -Hexane	Traces
H ₂ O	Undetd.

^a The amounts of by-products vary with experimental conditions and the range of values obtained for all experiments is given. ^b 5.9 when TMF was present. ^c 17.4 when H₂O was present.

The *n*-octane yields are highest, 7-8%, in the runs at low temperatures, 0° and -25°, and lowest, 3-4%, at 75°, with or without a hydrocarbon or

other solvent. Little or no ester, ketone or ether was present in the products of experiments carried out below 75°. The amount of aldehyde, however, is independent of experimental conditions. The highest yield of butyraldehyde and dibutyl ether is with tetrahydrofuran, and it is possible in this instance that these products arise from the solvent.

The alkylboronic acid, RB(OH)₂, the saponification product from incompletely oxidized trialkylborane, is not formed during the oxidation of undiluted or heptane-diluted trialkylboranes since it is insoluble in the oxidation reaction mixture and since there is no evidence of solids. Low yields of boronic acids were obtained in all experiments except one. A substantial yield of *n*-hexylboronic acid, 17%, is obtained in the oxidation of B(*n*-hexyl)₃ in the presence of considerable water. In only this case of the presence of water can a low total O₂ uptake, 73%, be correlated with incomplete oxidation of boron alkyl to boronate ester. Thus, water is an inhibitor for oxidation of the third boron-carbon bond. Johnson and Van Campen⁹ state that water inhibits the oxidation of the second boron-carbon bond as well as the third. They report that only 33% of the theoretical amount of oxygen is absorbed by B(*n*-butyl)₃ in the presence of water, and the boronite is the product. This work shows formation of the boronate with water present, and no borinic acid could be found in this or other experiments. Comparable by-products to those in B(*n*-butyl)₃ air oxidation are obtained in B(*n*-hexyl)₃ oxidation.

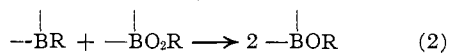
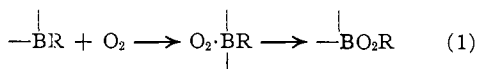
Discussion

The formation of a complex between oxygen and alkylboron compound as the first step in the air oxidation of alkylboron compounds has been suggested by Davies,⁴ Zutty,^{4,7} Johnson⁹ and Grummitt.¹⁰ The results, particularly with pyridine, where an inhibition of oxygen absorption at temperatures below 75° is observed, are consistent with the formation of such a complex. The decrease in total oxygen uptake in experiments with pyridine, water, H₃PO₄ and dimethylformamide present in the oxidation probably is due to the in-

(9) J. R. Johnson, *et al.*, *J. Am. Chem. Soc.*, **60**, 105, 111, 115 and 121 (1938).

(10) O. Grummitt, *ibid.*, **64**, 1811 (1942).

hibition of complex formation. Rearrangement of the complex then gives alkylperoxyboron compounds,^{4,7} eq. 1. The reaction of the peroxide with unoxidized boron alkyl bond, eq. 2, gives alkoxyboron compounds as described by Davies^{4,11} and Bawn.¹¹ Equations 1 and 2 are shown for the oxidation of one of the boron alkyl bonds, and the other two bonds may be considered oxidized or unoxidized.



The increasing difficulty of oxidation of successive bonds of trialkylboranes is attributed to decreasing Lewis acidity of the boron atom by the increasing number of oxygen atoms on the boron, which can form π -bonds with the boron atom.¹² The maximum alcohol yield at 0° demonstrates the greater stability of alkylperoxyboron compounds toward decomposition to by-products at lower temperatures, as discussed below, and allows more of the alkylperoxyboron compounds to participate in reaction 2. The maximum also indicates that reaction 2 can still proceed at an appreciable rate at this temperature, but reaction 2 must be slow at -25°. Since the alcohol yield is higher and the peroxide content during oxidation is lower in experiments without diluent present, reaction 2 must be favored by the higher concentration of alkylborane, and consequently reaction 2 appears to be an intermolecular instead of an intramolecular reaction. Davies⁴ has proposed an intramolecular reaction



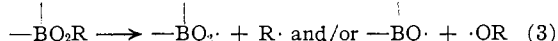
Davies⁴ and Zutty⁴ obtained high alkylperoxyboron yields only by working at high dilution which should slow reaction 2 if it is indeed intermolecular. Reaction 1, oxygen uptake, is not affected by dilution (Table I) and so the alkylperoxyboron compounds should accumulate in experiments at high dilution. The low alcohol yields with polar solvents suggest inhibition of reaction 2 and/or promotion of side reactions.

The nature of the by-products indicates that reactions of a free radical type are taking place. The possibility that all of these by-products arise from ionic reactions appears unlikely when one considers the lack of any major effect of polar solvents on the yields of by-products except for tetrahydrofuran and that both cleavage products (such as propane, hexane and propylene) and dimeric products (such as *n*-octane or 4-octanone) are formed. Some of the by-products are identical with products found in *n*-butyl hydroperoxide decomposition.¹³ An intermediate of peroxide type

appears to be the source of the by-products since the hydrocarbon by-products are formed primarily during the period of greatest peroxide formation and decomposition.

n-Butyl hydroperoxide is not considered to be the initial source of the by-products. Decomposition of this hydroperoxide produces neither the hydrocarbons found in this work (including the *n*-butane formed in 10-12 mole % yield) nor the 4-octanone or di-*n*-butyl ether, but does form as a major product hydrogen which was not found in this work. Hydroperoxide cannot reasonably form from an alkylborane without homolytic scission of an alkyl group or from an alkylperoxyboron compound without a hydrolysis step as shown by Davies.⁴ Consequently, *n*-butyl hydroperoxide is not the initial source of the by-products but could be a subsequent source. Di-*n*-butyl peroxide also is not considered to be the initial precursor of the by-products, since Rust¹⁴ has shown that the decomposition of *n*-butyl *t*-butyl peroxide gives only *n*-butyraldehyde and *n*-butyl alcohol among the products found in this work. Borate esters are stable to autoxidation,¹⁵ and cannot be the source of the by-products. We suggest that the by-products result from boron peroxybutyl compounds.

As cited above, the formation of boron peroxyalkyl compounds in trialkylborane oxidation is well established.^{4,11} Zutty⁴ showed that the boron peroxyalkyls decompose at increasing rates with increasing temperature, but the products of decomposition were not identified. Some evidence has been presented for the methyl radical as a product of dimethylboron peroxymethyl, $(\text{CH}_3)_2\text{BO}_2\text{CH}_3$, decomposition.¹⁶ It is postulated that boron peroxybutyl compounds are formed and decompose homolytically. The decomposition products are butyl and/or butoxy radicals. These



radicals can interact by known paths,¹⁷ to form essentially all of the by-products such as butane, butene and octane by disproportionation and dimerization of butyl radicals,^{17a} butyraldehyde by hydrogen abstraction from a butoxy radical,^{17b,14} and butyl butyrate, 4-octanone and butyric acid via a butyryl radical formed by hydrogen abstraction from butyraldehyde.^{13,17b} The dibutyl ether, similar to the formation of methyl ethyl ether from ethyl *t*-butyl peroxide,¹⁴ may arise by coupling of the butoxy and butyl radicals or by induced decomposition of a butylperoxyboron com-

pound by a butyl radical to produce a $-\text{BO} \cdot$ radical. The above hydrogen abstraction reactions and possibly still others cause the high butane/1-butene ratio. The presence of 2-butene may indicate the isomerization of an *n*-butyl radical to a

(14) F. F. Rust, F. H. Seubold and W. E. Vaughan, *ibid.*, **72**, 338 (1950).

(15) N. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(16) R. C. Petry, Ph.D. Dissertation, The Ohio State University, 1958.

(17) See especially: (a) E. S. Gould, "Mechanisms and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 692; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 273-280 and esp. p. 445.

(11) C. E. H. Bawn, D. Margerison and N. M. Richardson, *Proc. Chem. Soc.*, 397 (1959); A. G. Davies, D. G. Hare and R. F. M. White, *J. Chem. Soc.*, 1040 (1960); J. Furukawa, T. Tsuruta and Y. Nakayama, *J. Chem. Soc. Japan*, **63**, 876 (1960).

(12) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

(13) C. F. Wurster, L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **80**, 327 (1958).

sec-butyl radical albeit to a minor extent.¹⁸ The air oxidation of aromatic Grignard reagents also leads to by-products typical of free radicals¹⁹ as does the anodic oxidation of alkyl Grignard

(18) Some examples of alkyl free radical isomerizations are: J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960); C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958); D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 538 (1952).

(19) C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

reagents.²⁰ The other products of homolytic scission of the peroxyalkylboron compounds are $\text{-BO}\cdot$ and $\text{-BO}_2\cdot$ (reaction 3). These radicals may react to form -BOH compounds, also products of the oxidations.

(20) W. V. Evans, R. Pearson and D. Braithwaite, *ibid.*, **63**, 2574 (1941); W. V. Evans and R. Pearson, *ibid.*, **64**, 2865 (1942).

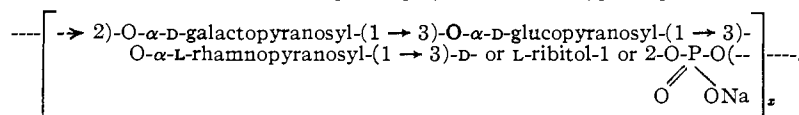
[CONTRIBUTION FROM THE INSTITUTE OF MICROBIOLOGY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, NEW JERSEY]

The Specific Polysaccharide of Type VI Pneumococcus. II.¹ The Repeating Unit²

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Evidence is given that the structural formula of the specific polysaccharide of type VI pneumococcus is:



Alkali converts the polymer to a monomer with a phosphate monoester linkage and this in turn is split by intestinal alkaline phosphatase into inorganic phosphate and a crystalline, non-reducing, chromatographically homogeneous galactoglucorhamnoribitol in 94% of the theoretical yield. The structure of the repeating unit was established by methylation, oxidation with periodate and degradation.

Because of the importance of the specific capsular polysaccharide of Type VI pneumococcus, S VI, for the understanding of the relation between chemical constitution and immunological specificity of the three related pneumococcal types II, V and VI, the study of its fine structure has been continued. In the first paper of this series¹ the following most probable formula was postulated: -E_4 or $2\text{-O-D-gal-}p\text{-(1}\rightarrow\text{3)-O-D-glu-}p\text{-(1}\rightarrow\text{3)-O-L-rham-}p\text{-(1}\rightarrow\text{1 or 3)-ribose-3 or 1-OPO(OH)-O}^-_x$. This conclusion was based on oxidation of S VI with periodate and hydrolysis with dilute alkali. The latter yielded non-reducing, dialyzable fragments which were homogeneous by paper electrophoresis and which contained galactose, glucose, rhamnose, ribitol and monoesterified phosphate. Additional data, resulting in a more explicit structure, are now given.

Experimental

Materials and Methods.—S VI was supplied by E. R. Squibb and Sons through the kindness of T. D. Gerlough. Lot 172 was purified as before,¹ but additional precipitations with methanol at low salt concentrations were necessary to remove N-containing impurities. Especial thanks are due Prof. Fred Smith for reference standards of methylated sugars.

Methoxyl was determined according to Steyermark.³ Infrared analyses were made with a Perkin-Elmer Model 21 recording infrared spectrophotometer at the Squibb Institute for Medical Research by Dr. N. H. Coy and Mr. C. Sabo. Thanks are also due Dr. R. H. Marchessault and Mr. N. W. Walter of the American Viscose Corporation for X-ray diagrams. Paper chromatographic analyses were carried out as before,¹ and the following additional solvents were

used: (A) 2-Butanone:H₂O azeotrope⁴ and (B) Benzene:EtOH:H₂O 200:47:15⁵

Reducing sugars were located with aniline hydrogen phthalate and non-reducing sugars or polyols with periodate spray reagents.⁶

Chemical Hydrolysis of the Phosphate Ester Group.—This was carried out before it was known that the phosphate ester could be completely hydrolyzed enzymatically. A solution of 1.0 g. of S VI, Ca⁺⁺ salt, in 80 ml. of H₂O was treated under N₂ with 10 ml. of ca. 0.4 N Ba(OH)₂ for 4 days at room temperature. This converted the phosphate diester linkages to monoesters. The pH was adjusted to 4.0⁷ with 2 N H₂SO₄ and the mixture heated in a glass-stoppered flask at 100°. Inorganic phosphate and reducing sugars as glucose were determined at 24 hr. intervals. After 24 hr., 59% of the P was liberated as inorganic phosphate and after 48 hr., 83% inorganic P and 7% of reducing sugar were formed. The reducing sugar rose to 13% after 72 hr., whereupon the hydrolysate was deionized with Dowex 50 and Duolite A4 and evaporated to dryness *in vacuo*. Neutral fragments, 0.811 g.; theoretical, 0.887 g. The residue was dissolved in water and separated on a 25 × 200 mm. charcoal-Celite column.⁸ Elution with 200 ml. of water and 100 ml. of 5% ethanol gave 64 mg. of material, $[\alpha]^{25}_D +41^\circ$ in H₂O, which indicated galactose and ribitol by paper chromatography. Elution with 300 ml. of 15–25% ethanol gave 598 mg. of a crystalline non-reducing substance, after drying *in vacuo* at 65°, $[\alpha]^{25}_D +110^\circ$, (*c* 1, in H₂O). Continued elution with 25% ethanol gave 85 mg. of reducing sirup, $[\alpha]^{25}_D +129^\circ$ (in H₂O). After recrystallization of the former fraction from isopropyl alcohol-water, the air-dry crystals melted with foaming at 140–145°. Further recrystallization from the same solvent, ethanol-water, or methanol gave a fusion point of 138–140°, unchanged by further crystallizations.

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(5) G. A. Adams, *Can. J. Chem.*, **33**, 56 (1955).

(6) J. A. Cifonelli and F. Smith, *Anal. Chem.*, **26**, 1132 (1954); J. Baddiley, J. G. Buchanan, R. E. Handschumacher and J. F. Prescott, *J. Chem. Soc.*, 2818 (1956); J. Baddiley, J. G. Buchanan and B. Carss, *ibid.*, 4138 (1957).

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(8) R. L. Whistler and D. F. Durso, *J. Am. Chem. Soc.*, **72**, 677 (1950).

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