in the absence of BH_4^- since slow attack of ether (a symmetrical cleavage agent) on the B_4H_{10}–R_2O intermediate would give H_3BOR_2 and $H_7B_3OR_2$. The former product would equilibrate with gaseous diborane above the solution. Removal of such gaseous B_2H_6 would drive the reaction to completion.

Furthermore, the possibility of unsymmetrical cleavage through the action of other reagents on this intermediate would not be eliminated. For example, OH^- or NH_2^-, which are known to favor unsymmetrical cleavage,[13] might well be expected to react on the intermediate to give unsymmetrical cleavage products (*i.e.*, $B_3H_8^-$ and H_2BOHOR_2).

Acknowledgment.—The support of this work by the National Science Foundation under grants NSF-G10372 and NSF-G21408 is gratefully acknowledged.

[13] R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3559 (1959); P. F. Winternitz, ref. 3, p. 178.

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Oxidation of Methylboranes at 77–170°K.

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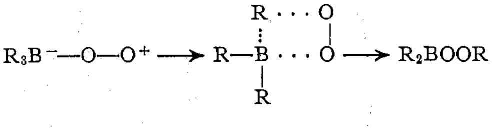
The oxidizability of $(CH_3)_3B$ (at 77 and 90°K.), 1,1-$(CH_3)_2B_2H_4$ (at 90°K.), $(CH_3)_4B_2H_2$ (at 170°K.), B_2H_6 (at 77°K.), and $(CH_3)_3P$ (at 147°K.) has been investigated in solution. Of these compounds only trimethylborane was found to be susceptible to oxidation, yielding dimethylboryl methyl peroxide in coordination polymeric form. Depolymerization to monomeric peroxide occurs upon warming. The results are consistent with a mechanism that involves transitory formation of an acid–base type adduct of trimethylborane with oxygen. The latter rearranges even at 77°K. to dimethylboryl methyl peroxide, $(CH_3)_2BOOCH_3$. A glass-and-metal high vacuum system was designed for low-temperature studies.

The susceptibility of boron alkyls to autoxidation is well known and the formation of peroxides,[1–6] boronates, borinates, and borates in the oxidative processes has been established. Brief discussions of this work with pertinent references, and of the mechanism of oxidation, have appeared in recent books.[7,8]

It has generally been assumed, following the initial suggestion by Johnson and Van Campen[9] and in analogy with the proposed mechanism of the oxidation of organomagnesium compounds,[10,11] that the primary step of oxidation involves the formation of a coordinate bond between the boron atom and oxygen.

$$R_3B + O_2 \longrightarrow R_3B^{-}\text{—}O\text{—}O^{+} \qquad (1)$$

Subsequent intramolecular migration of the alkyl group from boron to oxygen[3] has been proposed to yield the peroxides.



$$R_3B^{-}\text{—}O\text{—}O^{+} \longrightarrow \underset{\displaystyle R}{\overset{\displaystyle R\cdots O}{R\text{—}B\cdots O}} \longrightarrow R_2BOOR \qquad (2)$$

The inhibition of autoxidation by propylamine,[3] the lowering of reactivity upon vinyl substitution,[12] and the ineffectiveness of free radical trapping agents[3] are experimental findings which support the argument for the molecular mechanism of trialkylborane oxidation *in solution*. Reported experimental evidence for the existence of an oxygen coordination compound with tri-*n*-butylborane at 299°K.[4] could not be confirmed.[5]

The mechanism, which is consistent with the results of kinetic measurements on *gas phase* oxidation of trimethylborane, involves a radical chain reaction, initiated and terminated at the wall.[13,14]

It was thought to be of interest to investigate the oxidation of trimethylborane in solution at cryogenic temperatures. The energy of activation for the coordinate bond formation (reaction 1) can be assumed to be nearly zero. If the coordinate bond strength exceeds a few kcalories and the intramolecular rearrangement (reaction 2) is an activated process with a sufficiently high energy barrier ($E_{act} > 5$ kcal./mole), the oxidation could be halted at 77°K. after formation of the oxygen adduct. The exponential dependence of reaction rates upon temperature facilitates the preparation and study of metastable reaction intermediates at cryogenic temperatures.

It was also considered to be of interest to compare the autoxidative susceptibility of trimethylborane and of methylated diboranes under conditions which would not be expected to lead to oxidation reactions by a free

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[1] R. C. Petry and F. H. Verhoek, *J. Am. Chem. Soc.*, **78**, 6416 (1956).

[2] R. C. Petry, Ph.D. Dissertation, The Ohio State University, 1958.

[3] M. H. Abraham and A. G. Davies, *Chem. Ind.* (London), 1622 (1957).

[4] N. L. Zutty and F. J. Welch, *J. Org. Chem.*, **25**, 861 (1960).

[5] A. G. Davies, D. G. Hare, and O. R. Khan, *J. Chem. Soc.*, 1125 (1963).

[6] R. L. Hansen and R. R. Hamann, *J. Phys. Chem.*, **67**, 2868 (1963).

[7] W. Gerrard, "The Organic Chemistry of Boron," Academic Press, London and New York, 1961, p. 114.

[8] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 67.

[9] J. R. Johnson and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **60**, 121 (1938).

[10] C. Walling and S. A. Buckler, *ibid.*, **75**, 4372 (1953).

[11] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

[12] T. D. Parsons, M. B. Silverman, and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

[13] C. H. Bamford and D. M. Newitt, *J. Chem. Soc.*, 695 (1946).

[14] J. E. Coleman, Ph.D. Dissertation, The Ohio State University, 1959.

radical mechanism. The heat of dissociation of the BH_2B bridging unit, 28.5 kcal./mole in B_2H_6,[15] is sufficiently high to prevent dissociation and reactions of monomeric borane species at low temperatures. Diborane and its methyl derivatives do not possess vacant hybrid orbitals. Therefore these compounds would not be expected to undergo autoxidation at low temperatures if it entails coordination with a weakly basic compound, the oxygen molecule, in the primary step.

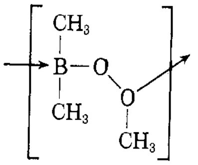
Results and Discussion

The oxidizability of trimethylborane, diborane, 1,1-dimethyldiborane, tetramethyldiborane, and trimethylphosphine was investigated at cryogenic temperatures in homogeneous solutions. The reaction temperatures and solvents had to be varied due to widely differing melting points and solubilities of these compounds. Trimethylborane was subjected to oxidation at 77°K. in ethane–propane and at 90°K. in chlorotrifluoromethane solution, diborane at 77°K. in ethane–propane solution, 1,1-dimethyldiborane at 90°K. in propane solution, tetramethyldiborane at 170°K. in methylcyclohexane solution, and trimethylphosphine at 147°K. in *n*-pentane solution.

Only one of the compounds, trimethylborane, was found to be susceptible to autoxidation at low temperatures. One mole of oxygen was consumed per mole of the borane in ethane–propane solution and also in chlorotrifluoromethane solution. The molar ratio of consumed oxygen to trimethylborane was independent of the excess amount of oxygen that was introduced into the system.

No visible change could be detected initially when oxygen was allowed to dissolve in solutions containing trimethylborane. After a period extending from a few minutes to 0.5 hr., and prior to achieving equilibrium oxygen pressure, a colorless solid product began to form. The viscosity of the solutions increased greatly and they acquired a gelatinous appearance. It was essential to start with low (<2 mole %) trimethylborane concentrations to have sufficiently fluid solutions for carrying the oxidations to completion.

After warming to room temperature the product was characterized as dimethylboryl methyl peroxide.[1,2] It is suggested that the polymeric low temperature product is poly(dimethylboryl methyl peroxide), containing the following repeating unit.



Coordinate bond formation by both oxygen atoms of the peroxy group would lead to cross linking, to which the gelatinous appearance is attributed. The dative bond strength of the coordination polymer is apparently very low. Dimethylboryl methyl peroxide is liquid at 155°K.,[2] and the vapor pressure data reported for temperatures above 233°K.[2] give 23.6 as the value of Trouton's constant.

Our conclusions regarding the structure of the low-temperature oxidation product are presently based upon its physical characteristics and identification of the material obtained upon warming. The alternative polymeric structure of identical composition, with peroxy bridges linking the boron atoms, is improbable because of the lack of energetically favorable boron bonding orbitals.

The vast difference in reactivity between trimethylborane and methylated diboranes clearly demonstrates that unoccupied sp^3 orbitals are essential for the autoxidation of methylboranes at low temperatures. These findings are consistent with and support the early thesis of Johnson and Van Campen,[9] which states that the primary step of the autoxidation of trialkylboranes consists of the formation of a coordination compound. The evidence also suggests that the latter is only of transitory existence even at 77°K. and rearranges to dimethylboryl methyl peroxide. Consequently, the energy required for the intramolecular rearrangement must be very low and the half-life of the oxygen addition compound quite short. We are currently developing techniques for following the course of the reaction spectroscopically at cryogenic temperatures to establish if the transitory existence of the oxygen adduct can be detected.

As represented in eq. 1, the reaction of trialkylboranes with oxygen in solution at low or moderate temperatures represents an example of reactions in which the oxygen molecule behaves as a weak Lewis base and not as a biradical. With regard to the base properties of molecular oxygen, it is of interest to note that it does not complex with boron trifluoride, which is normally a stronger Lewis acid than trimethylborane,[16] in nitrogen trifluoride solution at 77°K.[17] We also tested the acid properties of oxygen by bringing it into contact with trimethylphosphine in *n*-pentane solution at 147°K. The observed absence of a reaction indicates that the O_2 molecule does not possess pronounced acid properties.

Experimental

The Vacuum System.—A glass and metal high vacuum system[18] was designed for low-temperature studies. The glass components are connected to a metal manifold by means of bellows-sealed metal valves.[19] Amalgamation of the brass bellows is prevented by gold foil traps in manifolds which lead to mercury-containing components. The apparatus offers the advantage of utilizing grease- and mercury-free, easily manipulatable vacuum valves. The system is applicable for quantitative gas volumetric measurements.

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[15] R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).

[16] H. C. Brown and D. Gintis, *ibid.*, **78**, 5378 (1956).

[17] L. Parts, unpublished results of work conducted at Linde Division, Union Carbide Corporation. The author wishes to express appreciation for permission to quote these results.

[18] For an appendix to this publication, which provides a description of the vacuum system, order Document No. 8075 from the Chief, Photoduplication Service, Library of Congress, Washington 25, D. C., Auxiliary Publications Project, remitting $1.25 for microfilm (35-mm.) or $1.25 for photocopies.

[19] Available from Vacuum-Electronics Corp., Plainview, Long Island, N. Y.

The reactions were conducted in a low-temperature test tube of known volume, pictured in Fig. 1.

Solvents and Oxygen.—Ethane and propane were Phillips Petroleum Co. research grade hydrocarbons of 99.96 and 99.91 mole % purity, respectively. The binary mixture (50 ± 1 mole %) of these hydrocarbons[20] was degassed thoroughly at 77°K. prior to use as a solvent.

Chlorotrifluoromethane of 99.0% minimum purity (The Matheson Co., Inc.) was degassed and purified further by fractional distillation at 147°K.

n-Pentane (99.84 mole %) and methylcyclohexane (99.92 mole %) were research grade materials (Phillips Petroleum Co.).

Research grade oxygen (99.96 mole %, The Matheson Co., Inc.) was used.

Trimethylborane was prepared by the method originally described by Brown,[21] using 100% excess of methyl iodide and magnesium. The reaction was conducted in a helium atmosphere. The ethane formed in the preparation of the Grignard reagent was removed by purging the system prior to the addition of BF_3. The product was volatilized by passing a slow stream of helium through the reaction flask for 1 hr. while it was maintained at 120°, and it was condensed in a trap immersed in liquid nitrogen. Traces of solvent were later removed by vacuum distillation at 195°K. The yield of trimethylborane in the experiment conducted on 0.351 molar scale was 99%. It was contaminated by 2.3 mole % of ethane, as determined by mass spectrometric measurements.

The purification of trimethylborane *via* formation of the addition compound with triethylamine and the thermal decomposition of the adduct[21] can be conducted more conveniently at atmospheric pressure in helium atmosphere than under vacuum. The boiling points of trimethylborane (−20.2°) and of triethylamine (89.35°) differ widely and the degree of dissociation at elevated temperatures is high.[22,23] Transfer of triethylamine can be avoided with this modification, repetitive dissociation and condensation become unnecessary, and the pressurizing gas (helium) does not condense with the product.

Trimethylborane (90 mmoles) was dissolved in 200 mmoles of triethylamine and the mixture was degassed at 195°K. The system was pressurized with helium to 1 atm. and the reaction flask, equipped with an air-cooled condenser, was heated to 74–82° for 1 hr. Only the middle fraction of the distillate (65%) was used after it had been distilled twice from a trap at 195°K. into a receiver at 77°K. under vacuum. The vapor pressure of the product at 194.7°K. was 32.0 mm.; reported 31.6 mm.[24] The absence of detectable amounts of $(CH_3)_2BOCH_3$ and $CH_3B(OCH_3)_2$ in the product was ascertained mass spectrometrically.

Tetramethyldiborane was obtained by equilibration of a mixture of diborane and trimethylborane[25,26] and subsequent fractionation. To prevent formation of trimethylborane during the transfer of tetramethyldiborane, which occurs very rapidly with the pure product, 25 mole % of 1,1-$(CH_3)_2B_2H_4$ was allowed to remain in the sample of $(CH_3)_4B_2H_2$ which was subjected to oxidation.

1,1-Dimethyldiborane, also prepared by equilibration of diborane with trimethylborane,[25,26] had a vapor pressure of 9.53 mm. at 194.7°K.; reported[25] 10 mm. The product was also identified spectroscopically.[27]

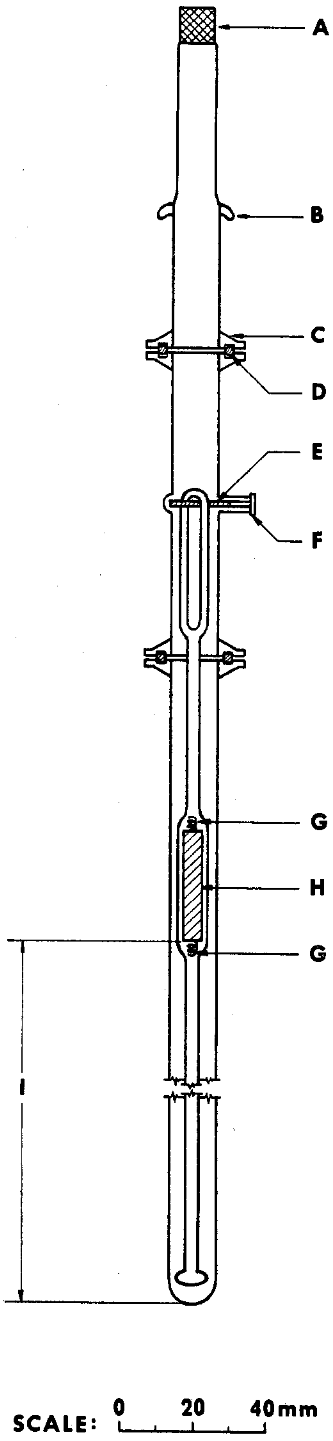

Fig. 1.—Low-temperature test tube: A, Kovar seal; B, hooks for supporting the low-temperature test tube; C, Delmar–Urry O-ring joint, 9-mm. i.d.; D, Viton O-ring; E, Teflon rod, 1.5-mm. diameter; F, glass plug, sealed into opening; G, springs; H, soft iron core, made from tubing, open slot on one side; I, 350 mm.

Diborane (Callery Chemical Co.) was purified by degassing at 77°K., followed by vacuum distillation from a trap at 147°K. into another at 77°K. The infrared spectrum of the purified product indicated the absence of higher boranes.

Trimethylphosphine was synthesized by the procedure described by Burg and Wagner.[28] The product apparently complexes with the magnesium halide. It was removed from refluxing butyl ether solution with a current of helium and collected in a trap immersed in liquid nitrogen. The yield after separation

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(20) H. M. Long and F. S. Di Paolo, private communication, established that an equimolar mixture of ethane and propane remains liquid at 77°K. Reference has previously been made to the use of this binary mixture as a cryosolvent for conducting chemical reactions: L. Parts and E. R. Shull, 138th National Meeting of the American Chemical Society, Sept., 1960.

(21) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

(22) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947).

(23) H. C. Brown and S. Sujishi, *ibid.*, **70**, 2878 (1948).

(24) C. H. Bamford, D. L. Levi, and D. M. Newitt, *J. Chem. Soc.*, 468 (1946).

(25) H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, **57**, 621 (1935).

(26) L. Van Alten, G. R. Seely, J. P. Oliver, and D. M. Ritter in "Borax to Boranes," T. Wartik, Ed., Advances in Chemistry Series, No. 32 American Chemical Society, Washington, D. C., 1961, p. 107.

(27) W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **34**, 476 (1961).

(28) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

TABLE I

ATTEMPTED OXIDATIONS

Compd. subjected to oxidn.	Amt., mmole	O_2 used, mmole	Equil. press., mm.	Temp., °K.
$(CH_3)_4B_2H_2$	0.39[a,b]	0.82	101.6	170
1,1-$(CH_3)_2B_2H_4$	0.23[c]	0.22	12.6	90
B_2H_6	0.45[d]	1.31	30.3	77
$(CH_3)_3P$	0.50[e]	1.13	133.9	147

[a] The reaction mixture also contained 0.13 mmole of 1,1-$(CH_3)_2B_2H_4$. [b] Solvent methylcyclohexane, 20.3 mmoles. [c] Solvent propane, 46.9 mmoles. [d] Solvent ethane–propane, 49.7 mmoles. [e] Solvent *n*-pentane, 23.7 mmoles.

from a small amount of butyl ether was 69%. The product was further purified *via* its silver iodide complex[29] and the vapor pressure after purification was 159.1 mm. at 273.2°K.; reported 161.0°,[28] 157.6[30] mm.

Oxidation of Trimethylborane at 77°K. in Ethane–Propane Solution.—The following experimental technique has been applied in the study of low-temperature reactions. A solvent having negligible vapor pressure at the temperature of the experiment was found for the compound to be oxidized. A homogeneous solution was prepared and oxygen was admitted into the low-temperature test tube. The reaction mixture was stirred until constancy of pressure was achieved. The amount of unreacted oxygen was calculated, using solubility data for the oxygen–solvent system at the temperature of the experiment. Also, the effective volume of the low-temperature test tube was determined and corrected for the volume of the suspension. Since the product was insoluble in the solvent, and the amounts of the reactants were small, the procedure yielded reproducible and accurate results.

Trimethylborane (0.446 mmole) was dissolved in an ethane–propane mixture, composed of 25.3 mmoles of ethane and 25.0 mmoles of propane, at 77.3°K. Oxygen (0.532 mmole) was introduced into the low-temperature test tube at an initial pressure of 56.41 mm. Stirring was started, oxygen absorption ensued, and the solution remained homogeneous for 30 min. while the pressure above the solution decreased to 15.47 mm. Subsequently the solution became turbid, more viscous, and the rate of oxygen absorption decreased. After 3.5 hr. the pressure was 2.68 mm. and the colorless, opaque suspension was allowed to stand overnight. Equilibrium pressure, 2.58 mm., was established. The amount of unreacted oxygen in the vapor phase and in solution was 0.024 and 0.068 mmole, respectively, and the amount consumed in the reaction was 0.440 mmole. The molar ratio of consumed oxygen to trimethylborane was calculated as 0.99.

The amount of oxygen consumed in the oxidation of trimethylborane at 77°K. was found to be independent of the initial oxygen-to-trimethylborane molar ratio. By varying it from 1.19 to 6.05, the molar ratio of consumed oxygen to trimethylborane remained constant (1.01 ± 0.02).

The product was identified spectroscopically upon warm-up. The solvent was removed by evacuation at 147°K. (methylcyclohexane slush bath). The remaining product was transferred into an infrared gas cell, and the spectrum was recorded at 40 and 5 mm. Absorption maxima in the 650–4000 cm.$^{-1}$ region were observed at the following frequencies: 798 (w), 845 (vw), 945 (w), 1030 (s), 1150 (s), 1159 (s), 1189 (s), 1290 (s), 1323 (s), 1342 (s), 1437 (m), 1483 (m), 2840 (w), 2940 (m), 2990 (s) cm.$^{-1}$. These frequencies are in agreement with those observed by Petry[2] for gaseous $(CH_3)_2BOOCH_3$. The infrared spectrum of the low-temperature reaction product also indicates the absence of detectable amounts of $(CH_3)_2BOCH_3$ and $CH_3B(OCH_3)_2$.

Oxidation of Trimethylborane at 90°K. in Chlorotrifluoromethane Solution.—Trimethylborane (0.999 mmole) was dissolved in 49.5 mmoles of chlorotrifluoromethane at 90°K., and oxygen (1.213 mmoles) was admitted to the low-temperature test tube. The reaction proceeded to completion in 3 hr.; however the reaction mixture was allowed to remain under oxygen pressure overnight. The final equilibrium pressure was 45.29 mm., and the amount of unreacted oxygen was 0.220 mmole.

The molar ratio of consumed oxygen to trimethylborane was 0.99. Observations made during this experiment were analogous to those described in the preceding experiment. The product appears to be polymeric also in CF_3Cl at 90.0°K.

Attempted Oxidation of Tetramethyldiborane, 1,1-Dimethyldiborane, Diborane, and Trimethylphosphine.—Homogeneous solutions of $(CH_3)_4B_2H_2$, 1,1-$(CH_3)_2B_2H_4$, B_2H_6, and $(CH_3)_3P$ were prepared in suitable solvents at temperatures indicated in Table I. Oxygen was introduced and the systems were allowed to equilibrate. Subsequently the oxygen pressure was measured over a period of several hours. In none of these experiments did oxidation occur.

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(29) D. Purdie, referred to by F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

(30) E. J. Rosenbaum and C. R. Sandberg, *J. Am. Chem. Soc.*, **62**, 1622 (1940).