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Oxidation of 1,1-Dimethyldiborane. Isolation and Characterization of 2,5-Dimethyl-1,3,4-trioxadiborolane[1]

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A study of the reaction between 1,1-dimethyldiborane and oxygen in the gas phase using a mass spectrometric–molecular leak technique is described. The major stable final product at 80° is 2,5-dimethyl-1,3,4-trioxadiborolane, $(CH_3)_2B_2O_3$. This species is isolated and characterized by mass spectral, infrared, and nuclear magnetic resonance spectrometric and vapor density measurements. Other physical data provided for the molecule include a melting point, vapor pressures, and the heat of vaporization. The mass spectral and nmr data are interpreted to indicate that the unexpected stability of this molecule is due to partial aromatic character.

Introduction

The ease of autoxidation of the boron hydrides and their organo derivatives is well known.[2-4] These reactions are frequently explosive and lead to the formation of stable boron oxide and carbon dioxide. It has thus been difficult to isolate partially oxidized products and reaction intermediates. The formation of peroxides and further oxidation products has been established for the various tributylboranes. Thus mono- and diperoxides have either been isolated or identified by titration of iodine liberated from iodide solution in the autoxidation of tri-*n*-butylborane,[5,6] tri-*sec*-butylborane,[7] triisobutylborane,[8] diisobutyl-*tert*-butylborane,[9] and 2-methylpentylborane.[6] Recent work has emphasized the kinetics and mechanisms of autoxidation. It has been established that many of these reactions are free-radical chain processes.[10,11] The gas-phase peroxide dimethylboryl methyl peroxide has been isolated by Petry and Verhoek[12] as a relatively stable intermediate in the gas-phase reaction between trimethylborane and oxygen. This species was observed to rearrange to the more thermodynamically stable dimethoxy(methyl)borane, a product analogous to that found by Johnson and Van Campen[13] and also by Abraham and Davies[5] in the oxidation of butylboranes. Parts and Miller[14] found that the oxidation of trimethylborane in solution at low temperature was similar to that in the gas phase. However, these workers found that under these conditions, 1,1-$(CH_3)_2B_2H_4$, $(CH_3)_4B_2H_2$, and B_2H_6 were not susceptible to autoxidation.

Of the unsubstituted boranes, detailed studies to identify intermediates and products have only been performed for BH_3L (L = CO or PF_3), B_2H_6, B_4H_{10}, and B_5H_9. A final product in the oxidation of B_5H_9,[15,16] B_4H_{10},[16] and BH_3L[16,17] and in the reaction of B_2H_6[18] with O_2 in an electrical discharge has been shown to be 1,3,4-trioxadiborolane, $H_2B_2O_3$, a cyclic molecule of C_{2v} symmetry.[19] Boroxine, $H_3B_3O_3$, has also been observed to be a product in the explosive oxidation of B_5H_9[20] and B_2H_6.[21] The only report of a substituted derivative of $H_2B_2O_3$ is that from our laboratory where small amounts of the dimethyl species $(CH_3)_2B_2O_3$ were observed mass spectrometrically in the reaction between $B(CH_3)_3$ and O_2 at 125°.[22] These observations were made using a mass spectrometric molecular leak technique which is described below.

This paper describes aspects of a study of the reaction between 1,1-dimethyldiborane and oxygen in the gas phase in which we report the isolation and characterization of 2,5-dimethyl-1,3,4-trioxodiborolane (Figure 1).

Experimental Section

Borane-oxygen mixtures may explode so extreme caution should always be observed in handling them.

1. Materials. Diborane was obtained from the reaction between anhydrous stannous chloride and sodium borohydride at 250° *in vacuo.*[23] It was purified by trap to trap distillation at −157°. Trimethylborane was prepared by the reaction of trimethyl borate (Alfa Inorganics) and trimethylalane (Alfa) in diglyme (Fisher Scientific) at 0–10° under a nitrogen atmosphere.[24] It was purified by distillation from a trap at −96° and its purity was checked by infrared and mass spectrometry. The diglyme was stored over lithium aluminum hydride and distilled before use at 73° and 15 Torr; the trimethylalane was used without further purification and the trimethyl borate was stored in a silica gel desiccator and distilled before use. Oxygen (research grade, Matheson Gas Products) was used without purification; $^{18}O_2$ (98% enriched) was obtained from Isomet Corp.

1,1-Dimethyldiborane was prepared by circulating a 5:1 mixture of diborane and trimethylborane through a coil maintained at 100°, and at total pressures up to 400 Torr, for 4 hr. The apparatus consisted of a glass coil attached, in a closed system, to a centrifugal gas-circulating pump utilizing a magnetic stirring bar[25] and separated

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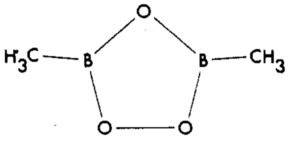

Figure 1.

from the vacuum system by a Teflon vacuum stopcock with Viton "O" rings. The major product of this reaction is 1,1-dimethyldiborane. Other species in the resulting mixture are monomethyldiborane, diborane, minor quantities of higher substituted boranes, and hydrogen. Unreacted diborane and hydrogen were pumped off at −157° and the 1,1-dimethyldiborane was isolated using vapor phase chromatography. Separation of the boranes by distillation in the vacuum line as described by Lehmann, Wilson, and Shapiro[26] did not yield products with chromatographic and mass spectral purity. The chromatographic separation was a modification of that described by Seely, Oliver, and Ritter[27] (see next section). A typical chromatogram shows three major fractions: B_2H_6, $CH_3B_2H_5$, and 1,1-$(CH_3)_2B_2H_4$ at approximate retention times of 108, 180 and 450 sec, respectively. Careful drying of the apparatus and pumping of the column for 24 hr before use were necessary for optimum recovery of diborane derivatives. A typical run yielded ~42% 1,1-$(CH_3)_2B_2H_4$, 29% $CH_3B_2H_5$, and 27% B_2H_6. The purity of the first of these was best checked by its infrared spectrum. The presence of two bands in the 2600-cm^{-1} region corresponding to the symmetric in-phase and asymmetric out-of-phase B–H stretching vibrations and the B–H out-of-plane bending vibration at 917 cm^{-1} was used as the criterion.[26,28] The commonly found impurity $CH_3B_2H_5$ showed a B–H out-of-plane bending vibration at 950 cm^{-1}.[29]

2. Apparatus and Techniques. All manipulations were carried out in a conventional Pyrex vacuum system with a background pressure of less than 5×10^{-5} Torr. All joints and stopcocks were lubricated with "Apeizon T" or "Fluorolube" stopcock grease (Fisher Scientific). Appropriate pressure calibrations were performed which allowed gas volumes to be measured and transferred. The lowest pressure measurements involved up to 5% inaccuracy although most measurements were much better than this.

a. **Chromatography.** A Varian Aerograph Autoprep, Model A790, preparative gas chromatograph was used, fitted with a stainless steel column, 305 cm long and with 0.4-cm i.d., packed with mineral oil on 30–60 mesh Johns-Manville Firebrick (38:100 weight proportion of mineral oil to packing). Helium flow rates of 25 cm^3/min at ambient temperature provided adequate separation of the methyldiboranes. The injection system was an all-glass vacuum system equipped with high-pressure stopcocks and a device whereby the He flow could bypass or flow through a U trap. Samples to be separated were condensed in the U trap, warmed to ambient temperature, and swept into the gc column by diverting the He through the trap. Effluent fractions were trapped in a separate system of bypassable glass coils with a minimum of "dead" volume.

b. **Mass Spectral Measurements.** All spectra were recorded on an AEI MS1201B spectrometer. One of the four independent inlet ports was modified so that reactions could be carried out in a reaction vessel adjacent to the ion source of the mass spectrometer. A somewhat similar system has been described previously.[16,30] The reaction vessel is shown in Figure 2. The Pyrex glass vessel has a volume of ~40 ml and is separated from the ionization chamber of the mass spectrometer by a small pinhole, made by sealing off the end of a piece of 0.5-mm i.d. Pyrex capillary tubing and re-forming the hole using a "Tesla" coil discharge. The size of the pinhole is adjusted to give reasonable sensitivity in the mass spectrometer. This allows pressures of up to 50 Torr to be maintained in the reaction vessel while generating pressures in the ion source of less than 5×10^{-6} Torr. The other end of the capillary tube protrudes into the ion source so that its extremity is as close as possible to the ion-source block and thus to the beam of ionizing electrons. Reactants and products thus enter the mass spectrometer through the pinhole. Pressure drop due to the "pumping out" effect is negligible under these conditions. In a typical run, one reactant is added to another at constant temperature or the reactants are mixed in the vessel at a temperature at which observable reaction does not occur and then the temperature is raised. During this process, the mass spectrum is continually scanned; thus providing a continuous monitor of the reaction. Consequently, intermediates with lifetimes of a few seconds may be observed during the reaction. In other experiments, products purified elsewhere were introduced directly into the mass spectrometer.

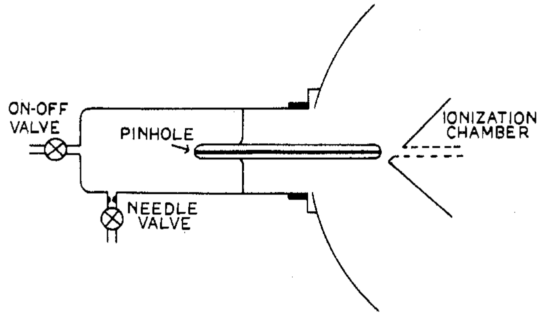

Figure 2. Mass spectrometric molecular leak reaction vessel.

c. **Other Spectral Measurements.** Infrared spectra were recorded in a 10-cm gas cell with KBr optics on a Perkin-Elmer 521 spectrophotometer. Tabulated values were calibrated against the polystyrene film spectrum. Proton nmr spectra were recorded on a Varian T-60 spectrometer and ^{11}B nmr spectra on a Varian HR-220 spectrometer.

3. Mass Spectral Study of the Oxidation of 1,1-$(CH_3)_2B_2H_4$. Pure 1,1-$(CH_3)_2B_2H_4$ (12 Torr) was introduced into the mass spectral inlet which had been baked at 100° under vacuum for several hours. If this were not done, small quantities of dimethylboric anhydride were observed which significantly increased upon heating the vessel. This impurity, resulting from reaction of the borane with traces of water on the walls of the vessel, was identified mass spectrometrically by the strong B_2 grouping at *m/e* 83, 82, and 81.[31] Oxygen was admitted very slowly and the mass spectrum was scanned over the range of 10–150 mass units. At ambient temperature, reaction between O_2 and 1,1-$(CH_3)_2B_2H_4$ was not observed. After a period of about 15 min when ~15–20 Torr of O_2 had been introduced, the process was stopped. Reaction was not observed after storage of the mixture under these conditions for several hours. If the reaction vessel were heated fairly rapidly, by means of heating tape wrapped uniformly around the vessel, the mixture ignited when the temperature was between 70 and 100°. Gas-phase boron products were not observed in this case. However, if the vessel were warmed slowly so that it took up to 20 min to reach 70°, there appeared prominent in the mass spectrum peak groupings at *m/e* 100 and 85 corresponding to B_2 species and one at *m/e* 58, all previously assigned to 2,5-dimethyl-1,3,4-trioxadiborolane.[22] Other features in the spectrum included trimethylboroxine[32] and species giving rise to peaks at *m/e* 73 and 57.[33] Diborane was also a product of this reaction. Under these conditions of pressure and temperature neither the BH_3 part of the 1,1-$(CH_3)_2B_2H_4$ molecule nor B_2H_6 itself reacts with oxygen.[34] The dimethyldiborane pressure was negligible after ~15 min. The final major boron-containing products observed after ~45 min were $(CH_3)_2B_2O_3$, $BH(OCH_3)_2$, $(CH_3)_3B_3O_3$, and B_2H_6. These species were identified by their mass spectra and in separate experiments by their infrared spectra.[35] The relative quantities of $(CH_3)_2B_2O_3$ and

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(33) The species giving rise to *m/e* 57 was unstable and not found in the final products of the reaction. The species giving rise to *m/e* 73 was shown to be dimethoxyborane, $HB(OCH_3)_2$. These features will be discussed in a subsequent paper: L. Barton and J. M. Crump, *Inorg. Chem.*, in press.

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$HB(OCH_3)_2$ depended upon conditions. If the temperature were increased too rapidly but less rapidly than necessary to cause ignition, larger quantities of $HB(OCH_3)_2$ were formed and little or no $(CH_3)_2B_2O_3$. Other minor products identified by their mass spectra were CH_4, CH_3OH, and H_2.

4. Chemical Properties of $(CH_3)_2B_2O_3$. The presence of the peroxide moiety in $(CH_3)_2B_2O_3$ was illustrated by cocondensing the latter with an excess of anhydrous hydrogen iodide. HI was prepared by dropping phosphoric acid onto hydriodic acid solution in the presence of red phosphorus. It was purified by trap to trap distillation at −78° and its purity was checked by infrared and mass spectrometry. When the cocondensate of $(CH_3)_2B_2O_3$ and HI was warmed to room temperature, the mixture slowly turned the characteristic dark red-brown color of I_2 indicating the presence of a peroxide linkage. A control experiment using methyl borate instead of $(CH_3)_2B_2O_3$ showed no color change.

The thermal stability of $(CH_3)_3B_2O_3$ is relatively high. Samples in deuteriochloroform solution sealed in nmr tubes were unchanged after storing at ambient temperature for 9 months. Gaseous samples heated to 100° for 12 hr showed up to 10% decomposition. The decomposition products were methane, boric oxide, and small quantities of an unidentified material. The absence of trimethyl borate and trimethylboroxine in the decomposition products was confirmed by infrared spectra. Condensation of $(CH_3)_2B_2O_3$ at low temperatures in clean glass surfaces always led to some decomposition to methane and other hydrocarbons, small amounts of hydrogen, and B_2O_3. Methane and hydrogen were identified in the mass spectrum of noncondensable gases. Up to 10% decomposition occurred on condensation. At room temperature, hydrolysis of $(CH_3)_2B_2O_3$ in the gas phase is very slow indeed. The only observable product is trimethylboroxine.

5. Recommended Synthesis of $(CH_3)_2B_2O_3$. The products of the above described equilibration of $B(CH_3)_3$ and B_2H_6 were pumped at −157° for 30 min to remove any hydrogen and unreacted B_2H_6. The resulting mixture of methyldiboranes, consisting mainly of 1,1-dimethyldiborane, was used without further purification. Into a well-taped 5-l. Pyrex flask, equipped with a "Fluorolube"-greased stopcock and a ground-glass joint, was introduced ~12 Torr of the borane mixture and ~20 Torr of oxygen. The mixture was allowed to mix for at least 30 min and was then placed in an oven at 85° for a further 30 min. The introduction of the cold flask ensured a relatively slow heating rate for the gaseous mixture. *Care should be taken during this operation. Use of pressures of borane greater than 15 Torr or too rapid heating of an incompletely mixed reaction mixture can result in hazardous explosions which may fracture the glass.* The mixture was then pumped at −157° to remove noncondensable gases and stored at this temperature pending further purification. This resultant mixture contained unreacted boranes (mainly $CH_3B_2H_5$) and $(CH_3)_2B_2O_3$, $HB(OCH_3)_2$, and $(CH_3)_3B_3O_3$ in the rough proportions 40:30:60:1, respectively, which varied from run to run. A crude separation was achieved by pumping at −111°; at this temperature $HB(OCH_3)_2$ could be slowly pumped off but satisfactory separation was not achieved by distillation. Final purification was achieved by introducing gas samples of about 0.6 mmol into the gas chromatograph. The column (described above) had to be pumped for 3 days at $<1 \times 10^{-4}$ Torr. A flow rate of 56 cm^3/min at ambient temperature was used. A well-defined peak with a retention time of 28.5 min was identified as pure $(CH_3)_2B_2O_3$ from its infrared spectrum (see below). The absence of the most likely impurity, $(CH_3)_3B_3O_3$, was demonstrated by the absence of the band at 1226 cm^{-1},[35a] one of the ring stretching modes of $(CH_3)_3B_3O_3$. A repetitive series of runs was necessary to accumulate quantities sufficient for the various spectral and other measurements necessary to characterize the material. Typically, a run in which ~3 mmol of borane mixture was used produced approximately 0.4 mmol of $(CH_3)_2B_2O_3$ in the product mixture representing yields in the range 17–26% based on conversion of 1,1-$(CH_3)_2B_2H_4$. The yield was reduced by a factor of 2 during the chromatographic purification resulting in overall yields of greater than 10%.

Results and Discussion

The initial identification of $(CH_3)_2B_2O_3$ in the mass spectral experiments described above was based upon the appearance of very prominent peak groupings at *m/e* 100, 99, 98 and 85, 84, 83 with the correct ratios for B_2 species, *i.e.*, 64:32:4. Only purification, by the means described above, enabled identification of other features in the mass spectrum since the initially formed product mixture contained species with common fragments, especially at the low-mass end of the spectrum.

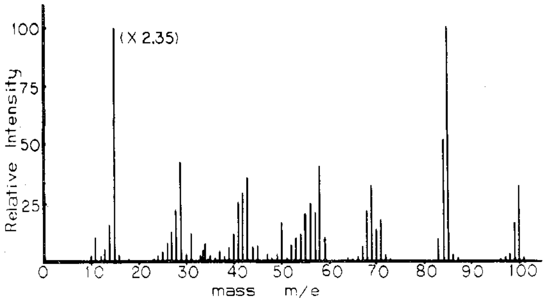

Figure 3. Mass spectrum of $(CH_3)_2B_2O_3$.

The spectrum of purified $(CH_3)_2B_2O_3$ is shown in Figure 3. It was found to be impossible to obtain mass spectra of $(CH_3)_2B_2O_3$, free of traces of $(CH_3)_3B_3O_3$. A well-defined and separated single peak, trapped from the chromatographic system under scrupulously anhydrous conditions, shown to be completely free of traces of $(CH_3)_3B_3O_3$ by its infrared spectrum and other techniques, nevertheless showed quantities of up to ~15% $(CH_3)_3B_3O_3$ in its mass spectrum. Thus the spectrum shown in Figure 3 was obtained by subtracting out the contributions due to $(CH_3)_3B_3O_3$, using the known spectrum of the latter and normalizing the various peaks relative to the base peak at *m/e* 111. This peak does not contain contributions from $(CH_3)_2B_2O_3$. The complete tabulated mass spectral data are found in Table I. Mass spectral runs using $^{18}O_2$ enable some ion assignments to be made. Results of the $^{18}O_2$ work and the assignments are listed in Table II. The above data are consistent with the molecular formula $(CH_3)_2B_2O_3$. The polyisotopic groupings at *m/e* 100 and 85 are in the correct ratio for B_2 species and isotopic substitution for ^{16}O by ^{18}O confirms the presence of three O atoms. Furthermore, the two major boron-containing fragments occurring at P^+ and $(P - 15)^+$ imply the loss of one methyl group.

The cyclic structure, shown in Figure 1, is consistent with mass spectral data for analogous systems. The four major high-mass ions in the mass spectrum of boroxine, $B_3O_3H_3$, are $H_3B_3O_3^+$, $H_2B_3O_3^+$, $HB_2O_3^+$, and $HB_2O_2^+$,[36] whereas the major high-mass ions for trimethylboroxine are $(CH_3)_3B_3O_3^+$, $(CH_3)_2B_3O_3^+$, and $CH_3B_2O_2^+$.[32] The spectra for the trioxodiborolane species are analogous: the major high-mass ions in the spectrum of 1,3,4-trioxadiborolane are $H_2B_2O_3^+$, $HB_2O_3^+$, $B_2O_3^+$, $HB_2O_2^+$ and HBO_2^+; thus the expected ions for $(CH_3)_2B_2O_3$ would be $(CH_3)_2B_2O_3^+$, $CH_3B_2O_3^+$, $CH_3B_2O_2^+$, and $CH_3BO_2^+$. These ions are observed, corroborating the proposed structure for this molecule.

Infrared spectra of pure samples of $(CH_3)_2B_2O_3$ in the range 3.1–40.0 μ are shown in Figure 4. Numerical data are found in Table III. Detailed vibrational analyses are available for the analogous systems $H_3B_3O_3$[37,38] and $H_2B_2O_3$.[39] Although there is some disagreement concerning the assignments of the observed infrared bands in $(CH_3)_3$-B_3O_3,[35a,40,41] it is useful to compare the bands in $(CH_3)_3$-

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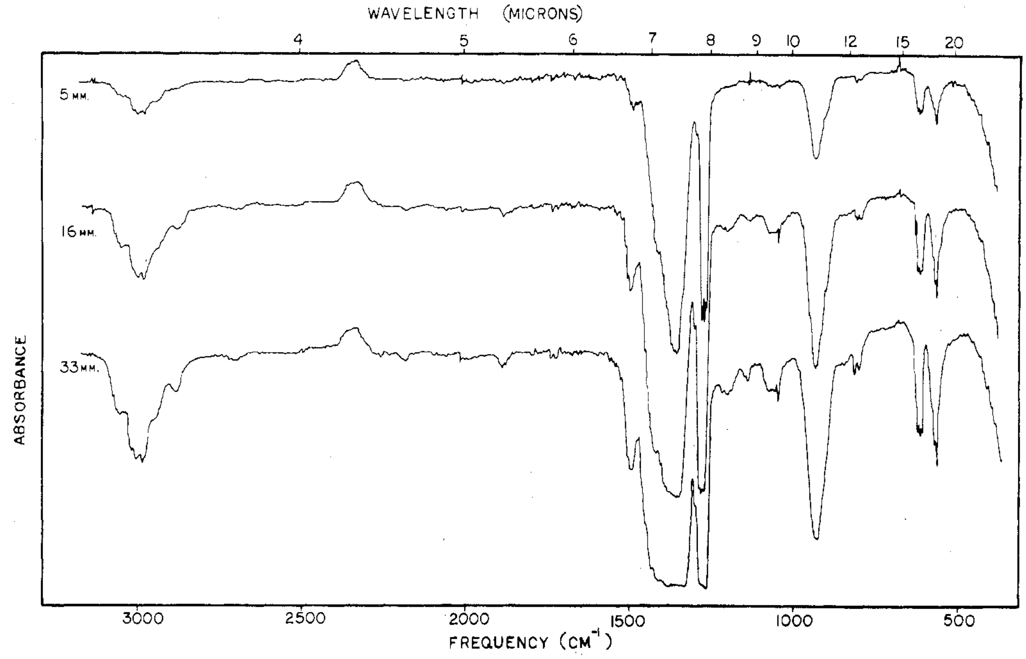

Figure 4. Infrared spectrum of $(CH_3)_2B_2O_3$ using KBr optics.

Table I. Mass Spectrum of $(CH_3)_2B_2O_3$

m/e	Intens	*m/e*	Intens	*m/e*	Intens
101	1.46	58	41.02	34.5	0.49
100	32.18	57	21.20	34	8.53
99	16.1	56	25.92	33.5	5.36
98	3.32	55	21.70	33	1.95
97	1.75	54	12.31	31	12.19
96	1.27	53	10.19	30	2.44
95	1.12	52	6.84	29	43.59
87	1.46	51	2.44	28	22.05
86	2.68	50	16.33	27	13.45
85	100.00	49	3.41	26	9.17
84	52.4	48	1.46	25	4.48
83	9.99	47	3.41	24	2.07
73	1.46	45	7.43	23	0.97
72	1.95	44	6.50	8	0.49
71	18.90	43	35.76	16	4.87
70	14.55	42	28.32	15	235.1
69	33.8	41	25.46	14	16.21
68	21.8	40	12.27	13	5.38
67	6.77	39	6.06	12	3.97
66	1.55	38	3.38	11	10.42
65	0.49	37	5.00	10	3.38
64	1.46	36	1.58		
59	12.68	35	2.44		

Table II. Mass Spectral Assignments for $(CH_3)_2B_2O_3$

Major peaks (*m/e*)		
^{16}O	^{18}O	Ion
100	106	$(CH_3)_2B_2O_3^+$
85	91	$CH_3B_2O_3^+$
69	73	$CH_3B_2O_2^+$
58	62	$CH_3BO_2^+$

Table III. Infrared Bands of 2,5-Dimethyl-1,3,4-trioxadiborolane

ν, cm^{-1}	Intensity[a]		ν, cm^{-1}	Intensity	
3040	m		1290	s	
3010	m		1275	vs	sp
2994	m		1268	vs	
2974	m	b	1263	vs	
2940	m		1207	w	
2875	m		1193	w	
2785	vw		1127	vw	
2180	vw		1055	m	sp
1877	vw		1037	m	
1730	vw		920	s	
1714	vw		892	m	
1515	w		835	vw	
1505	m		802	w	
1497	m		787	w	
1485	m		613	m	
1476	m		607	m	
1443	s		603	m	
1435	s		562	m	sp
1425	s	b	556	s	
1417	vs				
1410	vs				
1355	vs				

[a] Key: b, broad; sp, sharp; v, very; s, strong; m, medium; w, weak. Bands involving significant overlap are braced together.

B_3O_3 with our tentative assignments for $(CH_3)_2B_2O_3$. The intense bands at 1355 and 1268 cm^{-1} are the correct shape, are in the expected region for the in-plane ring stretching modes, and compare well with those at 1384 and 1226 cm^{-1} in $(CH_3)_3B_3O_3$. Of course the CH_3 wagging modes also occur in this region resulting in considerable overlap and possible uncertainties in assignment. The strong band at 920 cm^{-1} compares with that at 918 cm^{-1} in $(CH_3)_3B_3O_3$ and is assigned as the B-CH_3 asymmetric stretching mode. Fisher, *et al.*,[41] assigned the band at 783 cm^{-1} in $(CH_3)_3B_3O_3$ as the out-of-plane ring-bending mode. The equivalent bands in $H_3B_3O_3$ are at 380 and 425 cm^{-1}, respectively. It is thus likely that this band in $(CH_3)_2B_2O_3$ would be found in the region 800-900 cm^{-1}, so that the bands at 787-802 cm^{-1} may be this out-of-plane ring-bending mode. The out-of-plane BH bending modes in $H_3B_3O_3$ and $H_2B_2O_3$ are at 918 and 883 cm^{-1}, respectively, so that assignment of the band in $(CH_3)_2$-B_2O_3 at 556 cm^{-1} as the out-of-plane B-CH_3 bending mode is consistent with the assignment of Goubeau and Hummel for the band at 570 cm^{-1} in $(CH_3)_3B_3O_3$. The remaining prominent band at 607 cm^{-1} is probably the in-plane ring-bending mode which is expected to be found in this region: the corresponding values for $H_3B_3O_3$ and $H_2B_2O_3$ are found at 530 and 741 cm^{-1}, respectively. Thus the observed infrared spectrum of $(CH_3)_2B_2O_3$ is consistent with the proposed cyclic C_{2v} structure.

Vapor density measurements on a different samples weighing ~30 mg gave a mean value of 98.1 for the molecular weight compared with a value calculated for $(CH_3)_2B_2O_3$ of 99.7. Vapor pressure data obtained between −35.6 and +24° on freshly distilled samples are shown in Table IV. Values calculated using the least-squares equation $\log P = 9.297 - (2.130 \times 10^3)/T$ are also listed in the table. From the equation, the heat of vaporization is calculated to be 9.74 kcal/mol and the boiling point 58.8°. The melting point was determined to be −52.5 to −54.5° using a Stock apparatus and measuring temperature with an ammonia gas thermometer.

A proton nmr spectrum run in deuteriochloroform showed a single broad resonance at δ 0.56 ppm downfield from TMS. The methyl proton chemical shifts for trimethylboroxine and 2-methyl-1,3,2-dioxaborolane are at δ 0.39[42] and δ 0.17[43] ppm, respectively. The ^{11}B nmr spectrum run in chloroform showed a single broad resonance at δ −35.42 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ taken as zero. Literature values for the ^{11}B chemical shifts of the analogous systems $H_2B_2O_3$ and $(CH_3)_3B_3O_3$ are -33.6 ± 3.0[15] and −33.2[44] ppm, respectively.

Thus the physical data are consistent with the contention that we have isolated and characterized 2,5-dimethyl-1,3,4-trioxadiborolane. Mechanistic details and a discussion of other products are described in a separate paper.[45] The recommended synthesis from the impure borane mixture also yields unreacted $CH_3B_2H_5$ as a by-product. We have observed[34] that $CH_3B_2H_5$ reacts with O_2 at higher temperatures to produce lower yields of $(CH_3)_2B_2O_3$; however, since the reaction mixture tends to ignite unexpectedly in the temperature range 100–140°, heating the borane mixture to higher temperatures to cause all the methyldiboranes to react and perhaps obtain higher yields is not recommended.

This species, being only a partial oxidation product, is rather unusual in that it is a relatively stable molecule. Kotz, Vander Zanden, and Cooks[46] made some observations on the mass spectral fragmentation of boron-containing five-membered ring systems. Cyclic borenium ions are rare and are normally expected to be linear. Thus these ions are absent or are of less than 1% relative abundance in a whole series of dioxa-, dithia-, and diazaborolanes. This phenomenon is not observed in the 1,3,4-trioxadiborolane systems. Thus the borenium ions are the major fragments in the mass spectra of $H_2B_2O_3$ and $(CH_3)_2B_2O_3$. These molecules are six-π-electron systems and are probably stabilized by partial aromatic character. Increased π-electron density has been suggested by Coulson[47] for $H_2B_2O_3$ and by Armstrong and Perkins[48] for boroxines, both on theoretical grounds. A comparison of nmr data also implies evidence of ring current in these systems. The methyl proton chemical shifts for 2-methyl-1,3,2-dioxaborolane and dimethyoxy(methyl)borane are both found at δ 0.17 ppm downfield from TMS. These systems do not obey Huckel's $(4n + 2)$-π-electron rule and thus can be regarded as "nonaromatic" models. The methyl proton chemical shifts for both six-π-electron systems $(CH_3)_3B_3O_3$ and $(CH_3)_2B_2O_3$ are downfield at δ 0.39 and 0.56 ppm, respectively, suggesting some aromatic deshielding of the exocyclic protons by an induced ring current. Many other workers have proposed that boroxines are stabilized by partial aromaticity. The value for the ^{11}B chemical shift is in the expected region for this compound and is comparable to that in the analogous systems. The observation of $(CH_3)_3B_3O_3$ in mass spectra of "pure" $(CH_3)_2B_2O_3$ may be due to traces of water on the walls of the spectrometer, producing methylboronic acid which is readily converted to the anhydride under high vacuum. The explanation also may be that this is a more general phenomenon of cyclic boronates. It has been noted previously that inevitably one observes boroxines in the mass spectra of pure cyclic boronates.[49] Certainly the absence of trimethylboroxine in thermal decomposition products suggests that trimethylboroxine is not formed by simple thermal decomposition in the ion source of the mass spectrometer.

Table IV. Vapor Pressure Data for 2,5-Dimethyl-1,3,4-trioxadiborolane

Temp, °C	*P*, Torr		Temp, °C	*P*, Torr	
	Obsd	Calcd		Obsd	Calcd
24.0	129.7	135.2	−12.0	14.7	14.1
11.8	64.2	66.71	−23.0	6.55	6.11
5.5	46.4	45.3	−30.9	3.00	3.22
0	33.0	31.8	−35.6	2.10	2.31

It is interesting to note that derivatives of 1,3,4-trioxadiborolane have not been observed in the extensive studies of the oxidation of the higher organoboranes.[4] Presumably, this is due to the greater stability of the initially formed peroxides. Apparently the stability of borane peroxides decreases as the size of the substituent on boron decreases. Thus, although 1,3,4-trioxadiborolane is the major product in the oxidation of BH_3CO and BH_3PF_3, there is no direct evidence for intermediate peroxides although the results imply that they exist. Such peroxides in the oxidation of $1,1\text{-}(CH_3)_2B_2H_4$ are formed and will be discussed in a subsequent paper.[45] Another possible route to $(CH_3)_2B_2O_3$ is the oxidation of trimethylboroxine. It is known that boroxine reacts with oxygen to form 1,3,4-trioxadiborolane;[18] however, the analogous reaction with trimethylboroxine does not proceed to the corresponding trioxadiborolane.[50]

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Registry No. B_2H_6, 19287-45-7; $B(CH_3)_3$, 593-90-8; $1,1\text{-}(CH_3)_2B_2H_4$, 12070-96-1; O_2, 7782-44-7; $(CH_3)_2B_2O_3$, 31083-12-2.

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