ortho and para NH protons are magnetically equivalent. Compounds which have the substitutents, CN and OCN, provide good examples of the additivity effect (Table III). The chemical shift of an NH proton in $H(CN)_2B_3N_3H_3$ and $H(OCN)_2B_3N_3H_3$ is twice that observed for $H_2(CN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$, respectively. An even more interesting example involves the compound, $H(CN)(OCN)B_3N_3H_3$, which has both electron-withdrawing and electron-donating substituents. The observed chemical shift of the NH protons in $H(CN)(OCN)B_3N_3H_3$ is obtained from the algebraic sum of shifts for the CN and OCN groups. The data for compounds containing a chlorine are less clear. There does not appear to be an additivity effect for the substituent, chlorine, when the data for $H_2ClB_3N_3H_3$, $HCl_2B_3N_3H_3$, and $Cl_3B_3N_3H_3$ are compared. However, if one uses one-third of the relative chemical shift of $Cl_3B_3N_3H_3$, -0.03 ppm, as the effect of one chlorine on the nmr shift, a reasonable correlation is obtained for the shift in $H(Cl)(OCN)B_3N_3H_3$ and $H(Cl)(CN)B_3N_3H_3$ (Table III). It is interesting to note that with respect to the NH shift of $H_3B_3N_3H_3$, $Cl_3B_3N_3H_3$ exhibits a downfield shift, $HCl_2B_3N_3H_3$ is essentially unchanged, and $H_2ClB_3N_3H_3$ is shifted upfield. The existence of an additivity effect for the bromine is also unclear. However, an additivity effect is clearly not observed for those substituents, F and $N(CH_3)_2$, in which the ortho and para protons do not have the same chemical shifts. Additional work is necessary to establish the extent of this additivity effect. We attempted to look at $(OCN)_3B_3N_3H_3$ and $(CN)_3B_3N_3H_3$ but the compounds are not sufficiently soluble to obtain good spectra.

Acknowledgments. We wish to thank the National Science Foundation, Grant No. GP-20200, for financial support of this research.

Registry No. $H_2ClB_3N_3H_3$, 15061-65-1; AgNCO, 3315-16-0; AgCN, 506-64-9; $H(Cl)_2B_3N_3H_3$, 15259-40-2; $H(Cl)(CN)B_3N_3H_3$, 41380-16-9; $H(CN)_2B_3N_3H_3$, 41380-17-0; $H(Cl)(OCN)B_3N_3H_3$, 41380-18-1; $H(OCN)_2B_3N_3H_3$, 41380-19-2; $H(CN)(OCN)B_3N_3H_3$, 41380-20-5; $H_3B_3N_3H_3$, 6569-51-3; $Cl_3B_3N_3H_3$, 933-18-6; $H(Br)_2B_3N_3H_3$, 41380-21-6; $H(F)_2B_3N_3H_3$, 41380-22-7; $H[N(CH_3)_2]_2B_3N_3H_3$, 15599-21-0.

Contribution from the Department of Chemistry, University of Missouri–St. Louis, St. Louis, Missouri 63121

Oxidation of 1,1-Dimethyldiborane. Gas-Phase Peroxide Intermediates[1]

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The reaction between 1,1-dimethyldiborane and oxygen at 80° in the gas phase is described in which the major final stable product is 2,5-dimethyl-1,3,4-trioxadiborolane, $(CH_3)_2B_2O_3$. Mass spectrometric–molecular leak techniques indicate that the reaction proceeds *via* the formation of an unstable intermediate. The intermediate has been identified as dimethylboryl hydroperoxide, $(CH_3)_2BOOH$, which either rearranges intermolecularly to form dimethoxyborane or condenses, with the elimination of methanol and methane, to form $(CH_3)_2B_2O_3$. Evidence for this rearrangement is obtained from isotope substitution experiments in the mass spectral study. Evidence for the hydroperoxide is obtained from mass spectral and infrared spectrophotometric data and from chemical data.

Introduction

It is well established that the autoxidation of trisubstituted boranes proceeds by the formation of peroxides.[2] Samples of relatively stable mono-, di-, and triperoxyboranes have been prepared in autoxidation studies of various tributylboranes. It has been demonstrated recently that these reactions proceed *via* autocatalytic radical chain mechanisms.[3,4] However, in the case of the lower alkyl and unsubstituted boranes, the intermediate peroxides are less stable and much of the evidence for them is indirect. Studies of the autoxidation of triethylborane establish that peroxides are formed although these intermediate peroxides have not been characterized conclusively.[5,6] A well-characterized process is the oxidation of trimethylborane in which the initially formed dimethylboryl methyl peroxide slowly rearranges to dimethoxy(methyl)borane.[7,8] The oxidation of BH_3CO[9] and BH_3PF_3 to form $H_2B_2O_3$ has been shown to proceed *via* an intermediate which forms without the scission of the O–O bond in oxygen but the intermediates formed are too short-lived to have been observed by the techniques used.

Mechanistic information on the oxidation of partially substituted diboranes is lacking and the nature of any unstable intermediates in these processes is unknown. Indeed Parts and Miller[8] have reported that 1,1-$(CH_3)_2B_2H_4$, $(CH_3)_4B_2H_2$, and B_2H_6 are not susceptible to oxidation in solution at low temperatures. Bauer, Wiberley, and Sandvik[10] observed an intermediate in the oxidation of 1,2-$(C_2H_5)_2B_2H_4$ which appeared to be diperoxide.

This report describes mechanistic studies of the oxidation of 1,1-dimethyldiborane in the gas phase at temperatures up to 100°. Evidence shows that one intermediate is dimethylboryl hydroperoxide, $(CH_3)_2BOOH$, which rearranges or

(1) (a) Work supported by NSF Grant GP 11211. (b) Presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

(2) For reviews of peroxide formation in the autoxidation of boranes see A. G. Davies, *Progr. Boron Chem.*, 1, 265 (1964); T. G. Brilkina and V. A. Shushunov, "Reactions of Organometallic Compounds with Oxygen and Peroxides," Iliffe Books Ltd., London, 1969.

(3) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 17 (1967).

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(5) J. Grotevold, J. Hernandez, and E. Lissi, *J. Chem. Soc. B*, 182 (1971).

(6) L. Da-shun, H. Pao-tung, and C. Shou-chang, *Hua Hsueh Hsueh Pao*, 32, 43 (1966).

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(8) L. Parts and J. T. Miller, *Inorg. Chem.*, 5, 1446 (1966).

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condenses. The principal product is 2,5-dimethyl-1,3,4-trioxadiborolane, $(CH_3)_2B_2O_3$.

Experimental Section

Most of the techniques and procedures used in this study are described in the previous paper.[11] *Care is urged in handling these diboranes which can ignite unexpectedly if impure when exposed to air or oxygen.*

Diborane was prepared by the method of Jeffers by the reaction of sodium borohydride with stannous chloride at 250° *in vacuo*,[12] trimethylborane by the reaction between trimethyl borate and trimethylalane,[13] and 1,1-dimethyldiborane by the equilibration of a 5:1 B_2H_6-$B(CH_3)_3$ mixture at 100° for 4 hr. The 1,1-$(CH_3)_2B_2H_4$ was purified using gas chromatography. Dimethoxyborane[14] was made by cocondensing excess methanol with diborane, allowing the species to react for 1 min, pumping off the H_2, and distilling the product from −78 to −126°. The purity was checked by its infrared spectrum. Trimethylboroxine was made by the carbonylation of THF–borane in the presence of sodium borohydride. The purity was checked by infrared and mass[15] spectra. Oxygen (research grade, Matheson) was used without purification. $^{18}O_2$ (98% enriched) was obtained from Isomet Corp. $^{18}O_2$-$^{16}O_2$ mixtures were simply made by mixing the gases on the vacuum line. Anhydrous hydrogen iodide was made 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 checked by infrared and mass spectrometry.

Mass Spectral Studies. Reactions were carried out in a mass spectrometric–molecular leak system which has been described previously.[11] The system allows one to monitor continually a reaction by repetitively scanning the mass spectrum while the reaction proceeds in a Pyrex reaction vessel adjacent to the ion source of the mass spectrometer. The reaction vessel is separated from the ion source by a small pinhole. Pressures of up to 50 Torr in the reaction vessel generate ion source pressures of $\sim 5 \times 10^{-6}$ Torr, the pumping out rate during this period being negligible.

In a typical run 12 Torr of 1,1-dimethyldiborane and ~20 Torr of oxygen were added to the reaction vessel at ambient temperature. Reaction does not occur under these conditions. Mass spectra were run at this time to establish pressure–ion intensity calibrations to be used later. Then the temperature of the reaction vessel was increased by electric heating using heating tape and a powerstat. The rate of heating was critical in order to obtain good yields of $(CH_3)_2B_2O_3$ in this reaction, *viz.*, raising the temperature at a uniform rate to ~80–90° in a 20-min time period. Results from such a run are shown in Figure 1. The ions plotted were chosen so that pairs of ions from which a plot of I_a/I_b *vs.* temperature, where a and b represent different ions, was a straight line were eliminated. In such cases these ions are presumed to arise from fragmentation of the same molecular species and the ion with the higher relative intensity was plotted. Although there is some overlapping at the lower mass end of the spectrum, all the ion intensities plotted in Figure 1 are derived from ionization of different neutral molecules at the same time during the reaction. Omitted from the figure are all ions at m/e values less than and including 43 since there is such significant overlap that to distinguish independent variations of such ions in a representation such as Figure 1 would be difficult. One feature not shown in Figure 1 is that the peak at m/e 43 increases to a maximum after 10 min (T = 50°); it then decreases somewhat and subsequently increases gradually as the various products begin to form. Experiments were performed, on a small scale in the mass spectrometric inlet, in which O_2 98% enriched in $^{18}O_2$ was used, and the resultant spectrum was recorded to determine the number of O atoms per ion. In a separate set of experiments, reactions between 1,1-$(CH_3)_2B_2H_4$ and oxygen 50% enriched in $^{18}O_2$ were studied and the isotopic distribution of O in the base peaks of certain products was recorded. Mass spectra of independently prepared or separated species were introduced using a conventional room-temperature inlet system and their mass spectra were run.

Infrared Spectral Studies. Infrared spectra were run on Perkin-Elmer 521 or 337 grating spectrophotometers using a 10-cm gas cell with KBr optics.

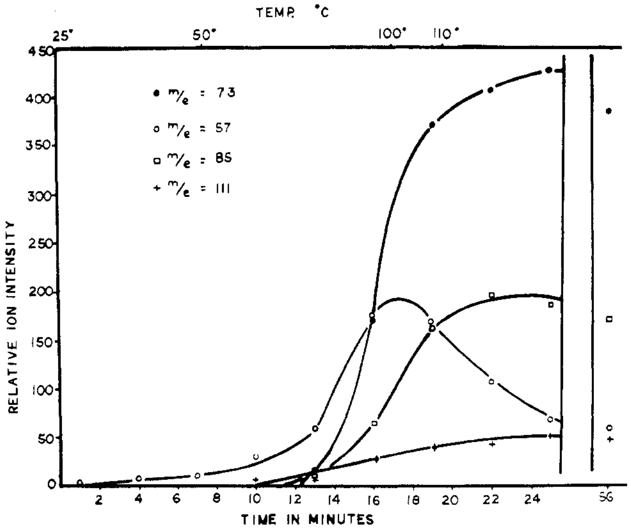

Figure 1. Curves showing the variations with temperature and time of the relative intensities of the major boron-containing ion peaks each arising from electron impact fragmentation of different products of the reaction between 1,1-$(CH_3)_2B_2H_4$ and oxygen.

One series of experiments involved heating reaction mixtures of O_2 and 1,1-$(CH_3)_2B_2H_4$ in the infrared cell in an oven, removing the cell at intervals, and rapidly running infrared spectra after varying lengths of time and at various temperatures up to 100°. The infrared cell, which maintained vacuum during this process, contained a "Fluorolube"-greased stopcock and the windows were sealed to the body by clamped neoprene "O" rings.

Characterization of Stable Products. The following species were identified in the final reaction mixture.

(a) $\mathbf{(CH_3)_2B_2O_3}$. 2,5-Dimethyl-1,3,4-trioxadiborolane was identified by its infrared and mass spectra. The complete characterization has been discussed.[11]

(b) $\mathbf{HB(OCH_3)_2}$. The results of the infrared spectral experiments, described above, showed that after the reaction had been completed and unreacted boranes pumped off at −127°, there remained in the spectrum a relatively sharp intense single absorption in the 2500-cm^{-1} region indicating the presence of >BH. Other features of the spectrum indicated the presence of $BOCH_3$ moieties. The mass spectrum of the reactant mixture showed major peaks at m/e 73 and 72, with ratios corresponding to a B_1 species. This grouping is a major peak in the spectrum of both $(CH_3)_2BOOCH_3$, a dimethylboryl methyl peroxide, and dimethoxy(methyl)borane, $(CH_3O)_2BCH_3$.[16] However, the absence of peaks at m/e 88, the parent ion in both these cases, rules out their presence. As noted previously[11] heating up the reaction mixture more rapidly in the mass spectral reaction vessel led to a product mixture containing very low yields of $(CH_3)_2B_2O_3$ and larger yields of the product with a base peak at m/e 73. This reaction mixture was readily obtained on a larger scale and the desired compound with the infrared absorptions at 2500 cm^{-1} and mass spectral base peak at m/e 73 was isolated by slow distillation from a trap at −111° to one at −127°. Its infrared spectrum was identical with that reported for dimethoxyborane, $HB(OCH_3)_2$, by Lehmann, Onak, and Shapiro,[17] the significant features being the B-H stretch at 2513 cm^{-1}, the B-O stretch at 1360 cm^{-1}, and the CH_3 deformation at 1493 cm^{-1}. The first and third bands were used to identify and quantify yields in product mixtures of runs performed in the infrared cell. The mass spectrum of the purified species was identical with that obtained from samples of $HB(OCH_3)_2$ prepared independently from B_2H_6 and CH_3OH. This spectrum is shown in Figure 2.

(c) **Methane and Hydrogen.** Methane was identified as a product of the reaction from the mass spectral results. Since the peak at m/e 15 was a very common ion, being derived from most of the species in the system, it was necessary to resolve the doublet at m/e 16 and observe the increase in abundance of the high-mass peak and verify that this was higher than the calculated ^{13}C contribution from the CH_3^+ ion. Methane was separately identified in the volatile fraction of the larger scale reactions, the peaks at m/e 16 and 15 being in the

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(11) L. Barton and J. M. Crump, *Inorg. Chem.*, **12**, 2252 (1973).
(12) W. Jeffers, *Chem. Ind.* (*London*), 431 (1961).
(13) J. Casanova, H. R. Kiefer, and R. E. Williams, *Org. Prep. Proced.*, **1**, 57 (1969).
(14) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **55**, 4023 (1933).
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(16) R. C. Petry, Ph.D. Thesis, The Ohio State University, 1958.
(17) W. J. Lehmann, T. P. Onak, and I. Shapiro, *J. Chem. Phys.*, **30**, 1215 (1959).

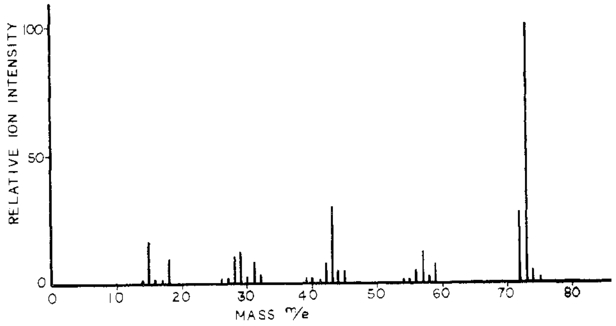

Figure 2. Mass spectrum of dimethoxyborane.

correct ratio of 100:89, respectively.[18] Hydrogen was identified in the mass spectrum of the product mixture.

(d) Diborane. Diborane was identified in the product mixture by its infrared and mass spectra. The absence of any possible gas-phase oxidation products of B_2H_6, *e.g.*, $H_2B_2O_3$ and $H_3B_3O_3$, was confirmed by their absence in the mass spectrum.

(e) Trimethylboroxine. This was identified in the product mixture of mass spectral runs by the characteristic B_3 peaks at *m/e* 126, 125, 124 and 111, 110, 109, respectively. The infrared studies showed that this species was only a very minor product of the reaction and that the larger amounts observed mass spectrally were probably formed in the ion source.

(f) Unstable Intermediate. The species giving rise to the peak at *m/e* 57 in the mass spectral runs was not a component of the final reaction mixture. Attempts to isolate this species were unsuccessful. Oxidations in the infrared cell were performed such that spectra were run when the peak at *m/e* 57 in Figure 1 was a maximum. The spectrum run under these conditions, *i.e.*, after heating up to ~80° in ~17 min, showed a fairly weak, moderately sharp absorption at 3690 cm^{-1} which disappeared slowly upon storing at room temperature for several hours. Condensation of the gaseous mixture caused rapid decomposition of the peak as did continuous heating of the infrared cell at 100°. Figure 3 shows the results of an experiment in which 12 Torr of 1,1-$(CH_3)_2B_2H_4$, and 20 Torr of O_2 were heated in the infrared cell in an oven at ~100°, and every 10 min the cell was removed and the infrared spectrum run. Only the portion of the spectrum between 3400 and 3800 cm^{-1} is reproduced since only in this region were spectral changes observed which could be assigned to the appearance of a short-lived species. A time scale is not meaningful since each transfer to and from the oven involves a significant cool-down and warm-up time in addition to an interruption in the heating of the reaction vessel so it is not included in Figure 3. Passing the reaction mixture through the gas chromatograph did not result in observation of any peaks attributable to the intermediate nor were attempts to isolate the species by high-vacuum fractional distillation successful. Apparently the intermediate once produced decomposed only slowly in the gas phase at room temperature, but condensation, passage through a gc column, and continued heating rapidly increased the decomposition rate. Experiments were also performed in which the products resulting from heating up the reaction mixture to ~80° in ~17 min were condensed with anhydrous hydrogen iodide gas. When the mixture was warmed to room temperature, it immediately turned to the dark red-brown iodine color. Control experiments using $(CH_3)_2B_2O_3$ and $B(OCH_3)_3$ were performed. In the former case, the iodine was observed but its rate of formation was much slower than in the above case. In the case of $B(OCH_3)_3$, the hydrogen iodide test was negative.

Reaction Stoichiometry. The initial stoichiometry was determined by comparing the rate of disappearance of O_2 with that for 1,1-$(CH_3)_2B_2H_4$ in the mass spectral runs. Calibrations of pressure *vs.* intensity for ions at *m/e* 32 for O_2 and *m/e* 54 for 1,1-$(CH_3)_2B_2H_4$ were performed. Overall stoichiometry, *i.e.*, moles of O_2 consumed per mole of borane, and also product distribution determinations were obtained from the reaction products from large-scale experiments in a 5 l. flask using both infrared absorbance and mass spectral intensity calibrations.

Results and Discussion

Isotope substitution experiments using $^{18}O_2$ indicated that the mass spectral base peaks corresponding to major participants in the reaction, 111, 85, 73, 57, and 43, were replaced by peaks at 117, 91, 77, 59, and 47, respectively. This confirms the presence of three, three, two, one, and two oxygen atoms, respectively, in these ions. These ions also had a peak distribution corresponding to the presence of three, two, one, one, and one boron atoms, respectively. The first three ions are reasonably assigned as arising from fragmentation of $B_3O_3(CH_3)_3$, $B_2O_3(CH_3)_2$, and $HB(OCH_3)_2$, respectively. Although the ion appearing at *m/e* 43, and thus assigned as BO_2^+, can be derived from the three species above, the reason for the initial large intensity of this ion prior to the formation of product is unclear.

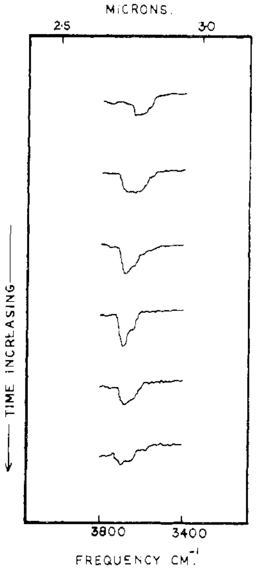

Figure 3. Infrared spectra in the region 3800-3400 cm^{-1} of a mixture of 1,1-$(CH_3)_2B_2H_4$ and O_2 during the course of reaction at about 100°.

The initial and overall stoichiometry determinations indicate that 1 mol of 1,1-$(CH_3)_2B_2H_4$ combines with 1 mol of oxygen. Overall reaction stoichiometry and material balance calculations indicate that 90% of the boron, initially present as 1,1-$(CH_3)_2B_2H_4$, is converted to B_2H_6, $(CH_3)_2B_2O_3$, and $H(BOCH_3)_2$. The ratio of $(CH_3)_2B_2O_3$ to $HB(OCH_3)_2$ is usually about 1:2 although this varies with the conditions of the reaction.

The unstable intermediate giving rise to the mass spectral peak at *m/e* 57 appears to be a peroxide. The absorption band at 3690 cm^{-1} in the infrared spectrum is comparable to the O-H stretch vibration at 3580 cm^{-1} for *tert*-butyl hydroperoxide. The spectrum of the latter was run for comparison. The hydrogen iodide experiments also indicate the presence of a peroxide. The major mass spectral peak at *m/e* 57 containing one O atom and probably one B atom is reasonably assigned as corresponding to $(CH_3)_2BO^+$. This indicates that the parent species is dimethylboryl hydroperoxide, $(CH_3)_2BOOH$. This species would be expected to fragment most facilely by the scission of the O-O bond. The parent ion, *m/e* 74, would be expected to be of low intensity and would overlap with the parent ion of dimethoxyborane. The major ion from electron impact fragmentation of dimethylboryl methyl peroxide is $(CH_3)_2BO^+$, whereas the parent ion intensity is only about 7% of this.[16]. Other important ions in the mass spectrum of $(CH_3)_2BOOH$ would occur at *m/e* 43 and 41, corresponding to BO_2^+ and $B(CH_3)_2^+$. These are expected to be of much lower intensity than $(CH_3)_2BO^+$ and to overlap with fragments of other reaction products. The mass spectral plot shown in Figure 1 indicates

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(18) "Selected Mass Spectral Data," Research Project 44, American Petroleum Institute, New York, N. Y., 1972.

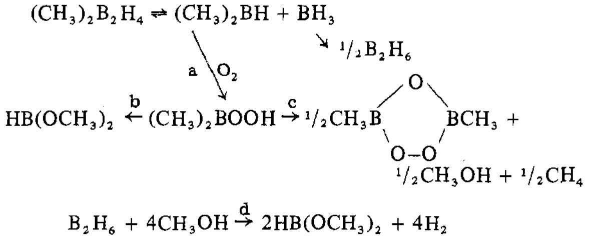
that the species producing the ion at *m/e* 57 is precursor to the final products of the reaction.

Information on the nature of the precursor to $(CH_3)_2B_2O_3$ can also be obtained from experiments using mixtures of $^{18}O_2$ and $^{16}O_2$ by measuring the isotopic distribution of the oxygen in the product molecule $(CH_3)_2B_2O_3$. There is no significant exchange of O_2 species at the temperature of this reaction. Results of such experiments are shown in Figure 4. In Figure 4, part a represents the distribution of O assuming complete statistical scrambling of the ^{16}O and ^{18}O atoms; part b shows the isotope distribution calculated if one of the O-O bonds in O_2 is retained in the $(CH_3)_2B_2O_3$ molecule. This latter result would arise if the precursor to $(CH_3)_2B_2O_3$ were to contain a peroxide moiety; part c shows the observed distribution. The results show that the isotopic distribution in the product for the $^{18}O_2$-$^{16}O_2$ oxidations is certainly nonstatistical and that the resultant distribution agrees, within experimental error, with the calculated distribution based on one of the O atoms being statistically distributed among the various molecules formed and the other two O atoms being derived from either an $^{16}O_2$ or an $^{18}O_2$ molecule. Examination of the resultant distribution in the product $HB(OCH_3)_2$ from the same experiments indicated that the distribution of O atoms was nearly statistical. The ratios observed for ions at *m/e* 77, 75, and 73 were 48.7, 100, and 68.4 respectively. The calculated values for a statistical distribution are 45, 100, and 58.2, respectively. These results imply that the oxygen atoms are nearly completely statistically scrambled in the formation of $HB(OCH_3)_2$. The deviation of the observed distribution from that expected from statistical scrambling of O atoms cannot be explained simply in terms of reasonable experimental error. Rather, one must assume that same process involving retention of O atoms from the same O_2 molecule may contribute to the formation of $HB(OCH_3)_2$ although not necessarily very greatly.

Thus, if as the data in Figure 1 suggest, the species giving rise to the major ion at *m/e* 57 is the precursor to both $(CH_3)_2B_2O_3$ and $HB(OCH_3)_2$, then alternative reaction pathways must be available for the decomposition of $(CH_3)_2BOOH$.

A plausible reaction scheme based upon the greater reactivity of the B-H bond than of the B-C bond and the general facile peroxide formation in the autoxidation of boranes can be proposed (see Scheme I).

Scheme I



Presumably insertion of O_2 into the B-H bond in reaction a is preceded by the formation of a loose adduct $(CH_3)_2BH\cdot\cdot\cdot O_2$, which subsequently rearranges to form the peroxide. This peroxide can then condense with the elimination of methanol and methane to form 2,5-dimethyl-1,3,4-trioxadiborolane by pathway b or rearrange to form dimethoxyborane by pathway c. These two reactions are shown to be thermodynamically favorable from bond energy calculations; pathway b is exothermic to the extent of 108 kcal/mol and pathway c, 153 kcal/mol.[19] A more favorable route to the formation of $HB(OCH_3)_2$ is provided by reaction d. This presumably accounts for the absence of methanol in the final reaction mixture. Reaction b is difficult to visualize. The $^{18}O_2$-$^{16}O_2$ results indicate that the rearrangement could be intermolecular and perhaps is a more general one involving the borane moieties also. Such a redistribution at 80° would lead to the thermodynamically controlled product $(CH_3O)_2BH$.[20] Whether trimethylboroxine is an important product in this reaction is unclear. One possibility is that the reaction $(CH_3)_2B_2O_3 \rightleftharpoons {}^2/_3(CH_3)_3B_3O_3 + {}^1/_2O_2$ occurs in the high-energy conditions of the ion source although previous work on the oxidation of $(CH_3)_3B_3O_3$[21] suggests that this equilibrium is not established readily in the reverse direction. This contrasts with the nonsubstituted boroxine which reacts rapidly with oxygen in the gas phase at ambient temperature to produce the corresponding trioxadiborolane.[22] At these temperatures and pressures diborane does not react with oxygen[23] and is thus a product of the reaction.

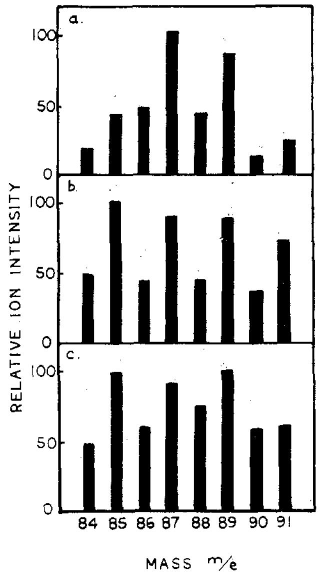
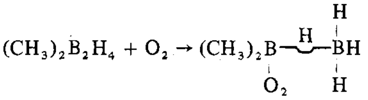


Figure 4. Mass spectral data for $(CH_3)_2B_2O_3$ illustrating the effect of using an $^{18}O_2$-$^{16}O_2$ mixture in the oxidation of $1,1\text{-}(CH_3)_2B_2H_4$. The figure includes (a) the calculated spectrum assuming statistical distribution of $^{18}O_2$ and $^{16}O_2$, (b) the calculated spectrum assuming nonstatistical distribution of $^{18}O_2$ and $^{16}O_2$, and (c) the observed spectrum. Mixture contained 46.6% $^{18}O_2$ and 53.4% $^{16}O_2$.

An alternative mechanism[24] for the initial stages of the reaction precludes the predissociation step. It is known that diboranes are not dissociated at all extensively in the vapor phase.[25] Thus one cannot rule out the formation of a very unstable singly bridged intermediate species



$$(CH_3)_2B_2H_4 + O_2 \rightarrow (CH_3)_2\underset{\displaystyle O_2}{B}\overset{H}{\frown}\underset{\displaystyle H}{\overset{\displaystyle H}{B}}H$$

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(19) Average bond energy values were taken from E. L. Muetterties, "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967, p 13; T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958, p 270.

(20) D. J. Pasto, V. Balasuboamaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, 8, 594 (1969).

(21) D. W. Wester and L. Barton, unpublished results.

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(23) L. Barton and J. M. Crump, to be submitted for publication.

(24) We are indebted to a referee for this suggestion.

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This species then would undergo rapid decomposition to give $(CH_3)_2B(H)O_2$ and BH_3, then B_2H_6. It has been suggested that both symmetrical and unsymmetrical cleavage of diboranes by nucleophiles proceeds *via* an initial step involving displacement of one bridge hydrogen to form a singly bridged species.[26]

The proposed mechanisms both involve the coordination of oxygen by a borane moiety analogous to that originally proposed by Johnson and Van Campen[27] and confirmed more recently by Davies and his coworkers.[2] The results indicate that reactivity toward oxygen under the gas-phase conditions is indicated by the series $BH_3 < (CH_3)_2BH \ll B(CH_3)_3$. Preliminary results indicate that CH_3BH_2 fits into the above series in the expected place.[23] This trend, although the reverse of Lewis acid strengths toward amines, can presumably be accounted for in terms of the relative stabilities of the boranes as dimers. Thus $B(CH_3)_3$ always has an empty p orbital whereas the ~36 kcal[28] involved in the reaction $B_2H_6 \rightleftharpoons 2BH_3$ increases the thermodynamic stability of the dimer. McCoy and Bauer[26] have shown that the bridge-breaking energy in substituted diboranes decreases with the number of substituents. However, the stability of the resultant peroxides, if indeed they are formed in all three cases, increases with increased substitution at boron and also with the size of the substituent on boron. Thus the peroxide is not observed as a intermediate in the oxidation of BH_3CO, although previous work undoubtedly suggests a reaction mechanism involving initial peroxide formation.[9] The stability of dimethylboryl methyl peroxide, however, is much higher, the half-life for rearrangement to the ester being about 60 days. The stability of the hydroperoxide formed in this study is apparently between the two above peroxides. The stability of these peroxides appears to be inversely related to their ease of condensation to form the trioxadiborolane as opposed to the rearrangement to form the dialkoxyborane species. Qualitative observations indicate that $(CH_3)_2B_2O_3$ is thermally more stable than $H_2B_2O_3$. Both species may be stored for periods of time without significant decomposition. Condensation to the solid at $-190°$ results in the deposition of a film of B_2O_3; warming and recooling to complete recondensation are not possible, indicating decomposition and the production of hydrogen and hydrocarbon respectively from $H_2B_2O_3$ and $(CH_3)_2B_2O_3$. This facile heterogeneous mode of decomposition is comparable to that of boroxine itself which completely disproportionates to boron oxide and borane when condensed. The oxidations of BH_3CO, BH_3PF, B_4H_{10}, and B_5H_9 all proceed heterogeneously.

Registry No. O_2, 7782-44-7; 1,1-$(CH_3)_2B_2H_4$, 12070-96-1; $(CH_3)_2BOOH$, 41557-63-5.

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Photochemistry of Vinyl-Substituted Germanium Derivatives of Transition Metal Carbonyls

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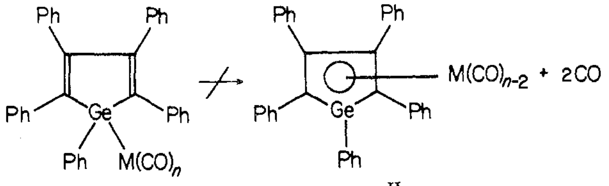
The preparation of vinyl-substituted germanium derivatives of transition metal carbonyls is reported. These compounds, $(CH_3)_2(C_2H_3)GeM$ ($M = Mn(CO)_5$, $Mo(CO)_3(\pi\text{-}C_5H_5)$, $Co(CO)_4$, $Fe(CO)_3NO$, $Co(CO)_2(NO)(CN)$, $Fe(CO)_2(\pi\text{-}C_5H_5)$, $Mn(CO)_4PPh_3$, $Co(CO)_3PPh_3$), are formally analogous to the corresponding σ-allyl compounds, $(\sigma\text{-}C_3H_5)M$. Photolysis proceeds with rupture of the germanium–metal bond to give complex mixtures from which compounds such as $Cp_2Mo_2(CO)_4$ (V), $Mn_2(CO)_{10}$, and μ-carbonyl-μ-dimethylgermyl-bis(cyclopentadienylcarbonyliron) (VII) may be isolated. The nmr parameters of the compounds are reported and correlated with the nucleophilicities of the metal anion, M^-.

Transition metal carbonyl groups appear to stabilize delocalized π systems. For example, π-allyl,[1] cyclobutadiene,[2] and trimethylenemethyl[3] complexes of transition metal carbonyls each contain a π system which is not stable as a free ligand. No compounds containing p_π-p_π bonds between carbon and its congeners have ever been isolated.[4] It is of interest to determine if a π system containing silicon, germanium, or tin might be sufficiently stablized by coordination to a transition metal carbonyl group to allow its isolation.

Curtis[5] found that σ-cyclopentadienyl analogs (I) did not form π-germacyclopentadienyl complexes (II) upon photolysis or heating. However, the presence of the substituent



I II (1)

phenyl groups may have seriously hindered the desired rearrangement.[6]

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