from both thermal stabilities and the closely related oxidative strengths. The thermal stabilities of these hexafluorides are in the following order

$$RuF_6 > RhF_6 > (PdF_6{}^{28})$$

$$OsF_6 > IrF_6 > PtF_6$$

$$OsF_6 > RuF_6,\ IrF_6 > RhF_6$$

The oxidizing power of these hexafluorides is of course in the reverse order as the following reactions show. Selenium tetrafluoride reduces platinum hexafluoride to the tetrafluoride, while osmium and iridium hexafluorides are reduced only to the pentavalent state.[29] Also ruthenium, rhodium, and platinum hexafluorides will oxidize xenon whereas osmium and iridium hexafluorides do not react.[30]

Further evidence for the increase in reactivity as we go across the periodic table comes from the reactions of osmium, iridium, and platinum pentafluorides with both selenium tetrafluoride and bromine trifluoride. The platinum compound is reduced to the tetravalent state while osmium and iridium form 1:1 adducts. Similarly, the reactions of the third row transition metal hexafluorides with nitric oxide support this systematic trend. Tungsten hexafluoride does not react,[31] osmium forms $NO^+OsF_6^-$,[32] but iridium and platinum form $(NO)_2IrF_6$[33] and $(NO)_2PtF_6$,[32] respectively.

Although there are relatively few chemical reactions that can be adduced as evidence, there is an obvious generalization that for higher fluorides thermal stability decreases and chemical reactivity increases with increase in atomic number for transition elements in the second and third rows. Also, it is easy to support the systematization that for subgroups of transition elements thermal stability of higher fluorides increases and chemical reactivity decreases as atomic number increases. It is not generally realized that for second and third row transition elements these differences become progressively greater in moving from a consideration of zirconium and hafnium, through niobium and tantalum, and on through molybdenum and tungsten to the elements of subgroups VII and VIII. It can be predicted confidently that these systematics can be made more rigorous as more work is done on the chemical reactivity of a wide range of transition metal fluorides.

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[28] No fluoride above PdF_4 is thermally stable.

[29] N. Bartlett and D. H. Lohman, *J. Chem. Soc.*, 619 (1964).

[30] J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 209 (1965).

[31] J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

[32] N. Bartlett, *Chem. Can.*, **15**, 33 (Aug 1963).

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Mass Spectrometric Study of Intermediates in the Oxidation of B_5H_9, B_4H_{10}, and BH_3CO[1]

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A mass spectrometric technique was used to follow the stoichiometry of oxidation of B_5H_9, B_4H_{10}, and BH_3CO as O_2 is slowly added to a borane sample at pressures between 5 and 20 mm. In the B_5H_9–O_2 reaction boroxine ($H_3B_3O_3$) is formed initially and further oxidation yields $H_2B_2O_3(g)$. Boroxine formed when B_5H_9 reacts with $^{16}O_2$–$^{18}O_2$ mixtures contains oxygen atoms in a statistical distribution while the oxidized product, $H_2B_2O_3$, contains oxygen in a nonstatistical distribution. Boroxine is not produced in the initial stage of oxidation of B_4H_{10} and BH_3CO, but $H_2B_2O_3$ produced with $^{16}O_2$–$^{18}O_2$ mixtures contains oxygen atoms in a nonstatistical distribution. Results of these isotope distribution experiments indicate that the precursor to $H_3B_3O_3$ (and $H_2B_2O_3$) in the B_5H_9–O_2 reaction is probably HBO or H_2BOH. In the B_4H_{10}–O_2 and BH_3CO–O_2 reactions the precursor to $H_2B_2O_3$ is probably H_3BO_2 (borane peroxide). Solids produced in the reaction of B_5H_9 and O_2 act as a catalyst to accelerate the decomposition of $H_3B_3O_3(g)$.

Introduction

Studies of the reaction of pentaborane-9 and oxygen have shown that the mechanism of oxidation is complex and is dependent on a number of factors including the order in which the reactants are mixed and the nature of the surface of the reaction vessel. Bauer and Wiberley[2] made an extensive investigation of the conditions of this system which lead to an explosive reaction. If O_2 is slowly added to gaseous B_5H_9 in Pyrex vessels, the reaction is nonexplosive at ordinary temperatures. Products of this reaction[3] include diborane, hydrogen, $H_2B_2O_3(g)$, and solid boron oxide. Complete oxidation is not realized under these condi-

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[1] Work supported by the Army Research Office, Durham, and the Advanced Research Projects Agency.

[2] (a) W. H. Bauer and S. E. Wiberley, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 115; (b) G. H. Lee, W. H. Bauer, and S. E. Wiberley, *J. Phys. Chem.*, **67**, 1742 (1963).

[3] J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959).

tions. The partially oxidized product, $H_2B_2O_3$, is also produced in a reaction of oxygen with boroxine ($H_3B_3O_3$).[4,5] The chemical behavior of $H_2B_2O_3$ is consistent with a molecule having a planar C_{2v} structure (*i.e.*, five-membered ring with O–O bond).[6] Formation of $H_2B_2O_3$ in the oxidation process suggests that a simple peroxide intermediate may be produced in the initial stages of the reaction. Evidence for the existence of peroxide intermediates in borane chemistry has been obtained in studies of the oxidation of trialkyl boranes.[7] The purpose of the present research effort was to obtain information on the nature of possible intermediates in the oxidation of gaseous boranes. The experimental approach was to observe incremental changes in the pressures of reactants and products as O_2 was slowly added to a second reactant. The changes were monitored by continuous sampling of the reaction mixture in a mass spectrometer. Boranes found suitable for this type of study were B_5H_9, BH_3CO, and B_4H_{10}. Diborane was not studied since it is not readily oxidized under the conditions of these experiments.[8]

Experimental Section

These boranes and their oxidation products are known to be explosive so caution should always be observed in their handling. Pentaborane-9 was obtained from the Callery Chemical Co. Nitrogen in the sample was removed by pumping the vapor through a liquid nitrogen trap. The condensed B_5H_9 was then redistilled *in vacuo* into a storage vessel at −196°. The vessel was warmed to −78° and pumped to remove any volatile impurity. The purity was checked by its infrared spectrum and vapor pressure. It was stored at −78°.

Borane carbonyl was prepared by a reaction of CO with solid boroxine. The procedure for the preparation has been described.[9]

Tetraborane was produced by pyrolysis of diborane. The latter was obtained from the reaction of stannous chloride with potassium borohydride *in vacuo* at 250°.[10] Diborane (~1 atm) containing trace amounts of higher boranes was maintained for 6 hr in the pyrolysis tube. The latter employed a hot zone at 120° and a cold zone at −78°. Yields of B_4H_{10} were always lower than those reported by Klein, *et al.*,[11] using a similar technique. Tetraborane was isolated from the other boranes produced by the normal methods of vacuum distillation; it was stored at −78° and redistilled before use.

Data for stoichiometry determination were obtained with the experimental arrangement shown in Figure 1. A cylindrical Pyrex vessel with a volume of about 40 ml served as the reaction chamber. Reactants and products enter a mass spectrometer through a small pinhole. With this arrangement it was possible to generate a pressure of $\sim 4 \times 10^{-6}$ mm in the ion source from a usual working pressure of ~30 mm in the reaction chamber. That there was no appreciable "pumping out" effect was shown by monitoring the major ion peak of argon at ~30 mm in the reaction vessel. After about 1 hr a pressure drop of only a few per cent was noted. At the other end of the reaction chamber was a capillary leak for the introduction of O_2 at a constant rate controlled by a pressure head of O_2. The mass spectrometer is a 10-in., 60°, direction-focusing instrument. In a typical run B_5H_9 was admitted at a pressure of 20 mm and oxygen was slowly added until reaction was complete. The process usually took about 10 min for a fast run and about 40 min for a slow run. During the course of the reaction the major ion peak of one of the reactants or products was monitored in the mass spectrometer. For the gases B_5H_9, B_2H_6, BH_3CO, B_4H_{10}, and H_2, ion intensity calibrations for a given pressure were performed so that pressures could be plotted directly. A white solid, deposited during the reaction, tended to block up the pinhole and the capillary leak. This demanded frequent calibration of the inlet leak rate. In another series of experiments, oxygen enriched in $^{18}O_2$[12] was used and the products were analyzed directly in the mass spectrometer. These oxygen mixtures were prepared by adding $^{16}O_2$ to the sample of the highly enriched $^{18}O_2$. The percentages of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ were determined by a mass spectral analysis before and after use. Under ordinary conditions, statistical scrambling does not occur in these mixtures because of the slow rate of isotopic exchange.[13]

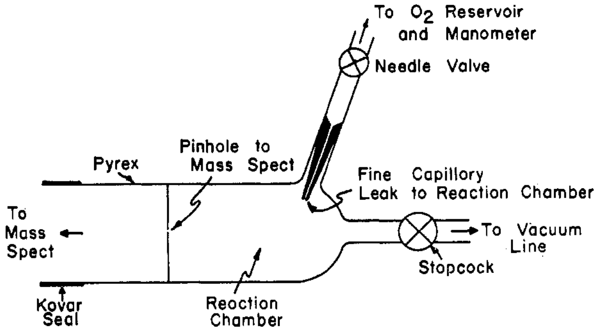

Figure 1.—Experimental apparatus.

Reaction Stoichiometry

The upper curve in Figure 2 illustrates the decrease in B_5H_9 pressure as O_2 is slowly added to the reaction vessel. In the initial stage of the reaction O_2 is entirely consumed. This was noted by monitoring the O_2^+ ion current as O_2 was added. However, a buildup of O_2 pressure within the reaction vessel was observed before the complete disappearance of B_5H_9. When the order of mixing was reversed and B_5H_9 was slowly added to the vessel containing 20 mm of O_2, reaction was not observed even when the pressure of B_5H_9 had reached 8 mm. This is the same effect that was pointed out by Bauer and Wiberley and indicates that the reaction may follow a heterogeneous path. This could result if the rate was influenced by competitive surface adsorption of the two reactants. The addition of ethylene to the reaction vessel, either before or after the pentaborane, was found to inhibit the reaction. An infrared spectrum of the white solid formed on the walls of the reaction vessel showed the substance to be mainly B_2O_3.[2a,14] A small amount of another solid was indicated by a broad absorption band at about 2600 cm^{-1}, which is the normal region for terminal B–H stretching vibrations. The structure of this band is different

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[4] S. K. Wason and R. F. Porter, *J. Phys. Chem.*, **68**, 1443 (1964).

[5] L. Barton, S. K. Wason, and R. F. Porter, *ibid.*, **69**, 3160 (1965).

[6] C. C. Costain, W. V. F. Brooks, and R. F. Porter, "The Microwave Spectrum and Structure of $H_2B_2O_3$," presented at the European Molecular Spectroscopy Conference, Copenhagen, 1965.

[7] (a) R. E. Petry and F. H. Verhoek, *J. Am. Chem. Soc.*, **78**, 6416 (1956); (b) L. Parts and J. T. Miller, *Inorg. Chem.*, **3**, 1483 (1964).

[8] (a) F. P. Price, *J. Am. Chem. Soc.*, **72**, 5361 (1950); (b) A. T. Whatley and R. N. Pease, *ibid.*, **76**, 1997 (1954); (c) E. Gobbet and J. W. Linnett, *J. Chem. Soc.*, 2893 (1962).

[9] S. K. Wason and R. F. Porter, *Inorg. Chem.*, **5**, 161 (1966).

[10] W. Jeffers, *Chem. Ind.* (London), 431 (1961).

[11] M. J. Klein, B. C. Harrison, and I. Solomon, Abstracts, 131st National Meeting of the American Chemical Society, Miami, Fla., April 1956, p. 4R.

[12] Obtained from Yeda Research and Development Co. Ltd., Rehovoth, Israel.

[13] R. A. Ogg and W. T. Sutphen, *J. Chem. Phys.*, **21**, 2078 (1953).

[14] T. A. Sidorov and N. N. Sobolev, *Opt. i Spektroskopiya*, **3**, 9 (1958).

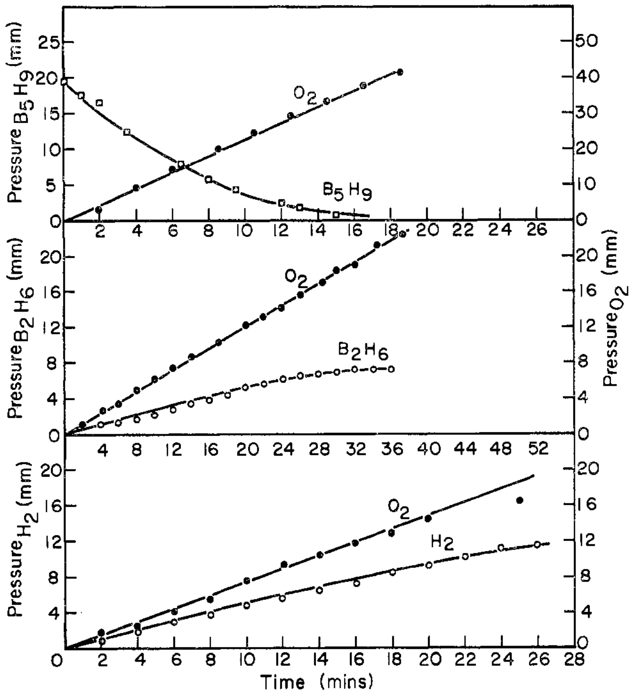

Figure 2.—Stoichiometry plots for the B_5H_9–O_2 reaction.

from that of any known boron hydride. The substance was involatile and not completely soluble in any of the usual solvents. It is presumed to be a high molecular weight boron hydride polymer or a mixture of the higher solid boron hydrides. This type of substance has been observed in the pyrolysis of B_2H_6[15] and its nature discussed elsewhere.[16,17]

Since the rate of disappearance of oxygen is rapid for a short time interval after it is added to B_5H_9 we can write

$$\frac{d(P_{O_2})}{dt} = -n_{B_5H_9}\frac{d(P_{B_5H_9})}{dt} \tag{1}$$

where $n_{B_5H_9}$ is the number of molecules of B_5H_9 reacting per molecule of O_2 in the initial stoichiometry. The value of $n_{B_5H_9}$ can be determined from the ratio of the slopes of the pressure plots in Figure 2. Similarly the initial rate of production of H_2 and B_2H_6 may be related to the rate of O_2 addition by the expressions

$$\frac{d(P_{O_2})}{dt} = n_{H_2}\frac{d(P_{H_2})}{dt} \tag{2}$$

$$\frac{d(P_{O_2})}{dt} = n_{B_2H_6}\frac{d(P_{B_2H_6})}{dt} \tag{3}$$

where n_{H_2} and $n_{B_2H_6}$ are the number of molecules of H_2 and B_2H_6, respectively, produced per molecule of O_2 reacting. These quantities were evaluated from the ratios of limiting slopes of pressure *vs.* time plots shown in Figure 2. A summary of the results is given in Table I.

Mass spectral and infrared observations established that gaseous $H_3B_3O_3$ and $H_2B_2O_3$ were both products in the B_5H_9–O_2 reaction. Relative changes in the abundance of these species were noted from changes in the ion intensities *m/e* 83 (for $H_3B_3O_3$) and *m/e* 71 (for $H_2B_2O_3$) as O_2 was added to B_5H_9. These effects are illustrated in Figure 3.

Table I

Stoichiometry Data for the B_5H_9–O_2 Reaction

$P_{B_5H_9}$, mm	O_2 flow rate, mm/sec	$\frac{-d(P_{O_2})}{d(P_{B_5H_9})}$	$\frac{d(P_{O_2})}{d(P_{B_2H_6})}$	$\frac{d(P_{O_2})}{d(P_{H_2})}$
17.2	0.50	1.45		
17.3	2.28	1.49		
24.3	0.94	1.45	2.1	
18.7	0.53		2.5	
17.4	3.14		2.3	
18.8	0.60		3.0	
20.0	6.00			
21.2	0.66			1.39
20.7	1.33			1.45

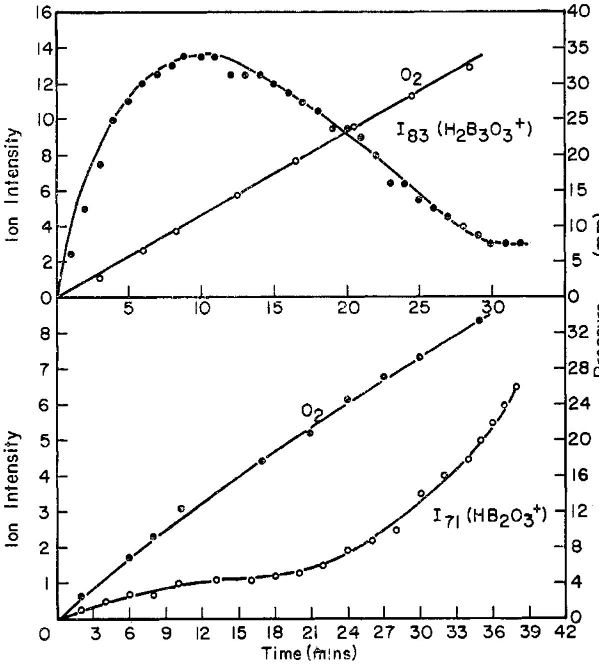

Figure 3.—Ion intensity *vs.* time plots for the appearance of $H_3B_3O_3$ (*m/e* 83) and $H_2B_2O_3$ (*m/e* 71) for the B_5H_9–O_2 reaction.

With the data from Table I and the material balance with respect to boron and hydrogen we may write for the initial stoichiometry in the B_5H_9–O_2 reaction.

$$B_5H_9 + 1.450O_2 \longrightarrow 0.72B_2H_6 + 1.04H_2 + 0.46{\pm}0.07H_3B_3O_3 + 0.54{\mp}0.07B_2O_3 + 1.26{\mp}0.22BH_{1.2\mp0.2} \tag{4}$$

Uncertainties assigned to $H_3B_3O_3$ and B_2O_3 arise largely because of the unknown composition of the solid borane. Recent literature[17] indicates that this substance probably has a composition between $BH_{1.0}$ and $BH_{1.4}$. An intermediate composition was assumed in eq 4.

In Figure 4 the upper curve illustrates the decrease in BH_3CO as O_2 is slowly added to the reaction vessel. As in the case of B_5H_9 both B_4H_{10} and BH_3CO appear to react with O_2 heterogeneously. For both it was possible to build up a relatively high concentration of oxygen before the complete disappearance of the borane.

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(15) J. R. Morrey, A. B. Johnson, Y.-C. Fu, and G. R. Hill, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 157.

(16) B. Siegel and J. L. Mack, *J. Chem. Educ.*, **34**, 314 (1957).

(17) For references see: W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

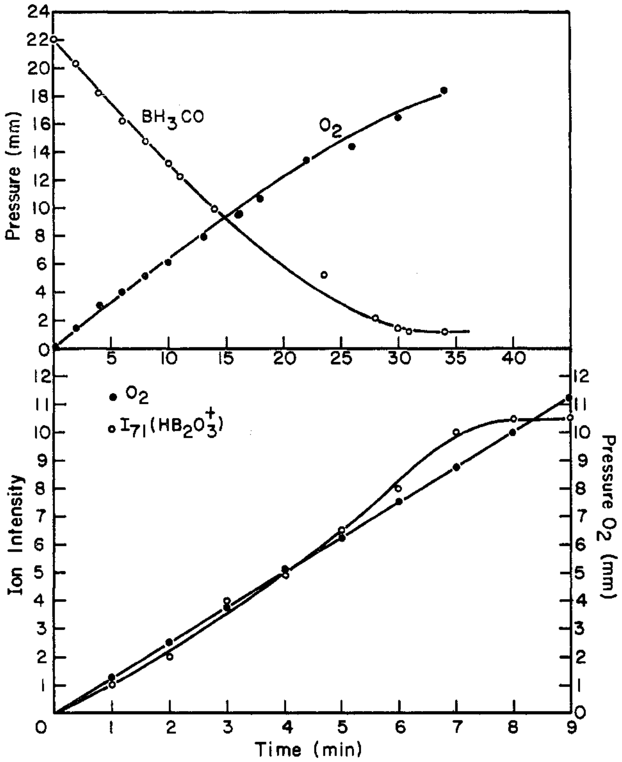

Figure 4.—Stoichiometry plots for the BH_3CO–O_2 reaction.

On reversing the order of mixing, reaction was not observed. The lower curve in Figure 4 illustrates that $H_2B_2O_3$ is an initial reaction product in the reaction of O_2 with BH_3CO. The initial stoichiometry was also determined by observing the infrared spectra of the gaseous reactants and products after addition of a small quantity of O_2 to BH_3CO. Pressure calibrations were made against BH_3CO, B_2H_6, and $H_2B_2O_3$ so that allowance could be made for impurities, decomposition products, and unreacted material. The results are summarized in Table II. From the infrared observations, eq 5 is formulated. A more general

$$BH_3CO + 0.73{\pm}0.03O_2 \longrightarrow 0.14{\pm}0.01H_2B_2O_3 + CO + 1.18{\mp}0.33H_2 + 0.35{\mp}0.2B_2O_3 \quad (5)$$

equation is

$$BH_3CO + {}^3/_4O_2 = \frac{1-\alpha}{2}H_2B_2O_3 + CO + H_2 + \frac{\alpha}{2}(H_2 + B_2O_3) \quad (6)$$

where α is the fraction of the maximum possible yield of $H_2B_2O_3$ either disproportionating to, or directly formed as, $H_2 + B_2O_3$.

TABLE II

STOICHIOMETRY DATA FOR THE BH_3CO–O_2 REACTION

P_{BH_3CO}, mm	Method of measurement	O_2 flow rate, mm/sec	$\frac{-d(P_{O_2})}{d(P_{BH_3CO})}$
22.2	Mass spectrometry	0.60	0.78
9.4	Mass spectrometry	0.59	0.58[a]
20.2	Mass spectrometry	0.14	0.59[a]
		O_2 added, mm.	
13.6	Infrared	7.7	0.75
10.7	Infrared	3.7	0.70
16.3	Infrared	13.3	0.81

[a] Not corrected for B_2H_6.

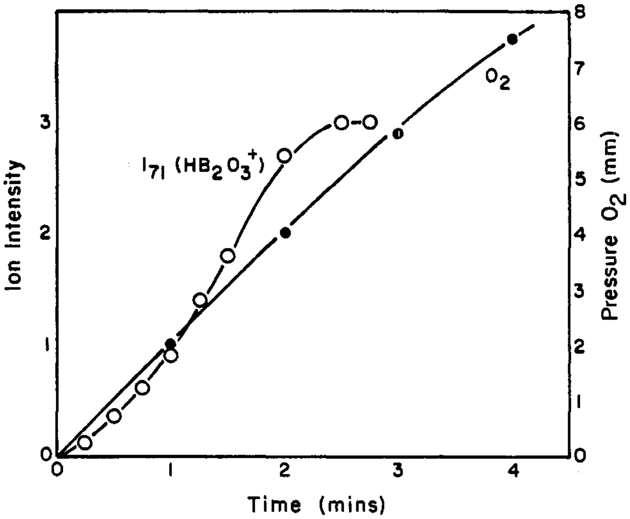

Figure 5.—Stoichiometry plots for the B_4H_{10}–O_2 reaction.

Since the reaction of B_4H_{10} with O_2 was not instantaneous, initial pressure *vs.* time plots were unsatisfactory for determining the stoichiometry. The stoichiometry was checked by measuring the amounts of reactants and products consumed or produced during the reaction. Since all the gaseous products were produced in the initial stages of the reaction, such a means of determining the reaction stoichiometry is feasible. Boroxine was not produced in this reaction but $H_2B_2O_3$ was an initial product (see Figure 5). The infrared spectrum of the solid produced in this reaction indicated the presence of a high molecular weight boron hydride polymer as well as boron oxide. The results are summarized in Table III. From these observations, we can formulate a general equation analogous to that in the BH_3CO–O_2 reaction

$$B_4H_{10} + {}^3/_2O_2 = 2H_2 + {}^1/_2B_2H_6 + (1/x)B_xH_x + (1-\alpha)H_2B_2O_3 + \alpha(H_2 + B_2O_3) \quad (7)$$

TABLE III

STOICHIOMETRY DATA FOR THE B_4H_{10}–O_2 REACTION

$P_{B_4H_{10}}$, mm	Method of measurement	$\frac{d(P_{O_2})}{d(P_{B_4H_{10}})}$	$\frac{d(P_{H_2})}{d(P_{B_4H_{10}})}$	$\frac{d(P_{B_2H_6})}{d(P_{B_4H_{10}})}$
6.8	Infrared	1.61	1.95	0.55
5.3	Infrared	1.65	1.64	0.63
6.5	Mass spectrometry	1.46		0.43
4.7	Mass spectrometry	1.66		0.33
14.9	Mass spectrometry		1.8	
11.1	Mass spectrometry		1.9	

Oxidation with $^{18}O_2$–$^{16}O_2$ Mixtures

Isotopic distributions of ^{16}O and ^{18}O in oxidized products obtained when enriched $^{18}O_2$ mixtures were used in place of ordinary oxygen were observed from changes in mass spectral patterns. For $H_3B_3O_3$ and $H_2B_2O_3$ the *m/e* ranges between 80 and 90 and 69 and 78, respectively, were monitored. The normal isotopic distribution for these species is known from experiments with ordinary oxygen.[5,18] Isotopic distributions were observed for $H_3B_3O_3$ and $H_2B_2O_3$ produced in the B_5H_9–O_2 reaction and for $H_2B_2O_3$ produced in the BH_3CO–O_2 and B_4H_{10}–O_2 reactions. Results of these experiments are shown in Figure 6 (I, II, III, and IV, respectively).

Decomposition Behavior of Boroxine

The rate of decomposition of the intermediate, boroxine, was studied by observing the decrease in ion intensity for *m/e* 83 as a function of time and concentration. Maximum yields of boroxine corresponding to the plateau in Figure 3 were obtained by adding one part of O_2 to about three parts of B_5H_9. In certain runs, ion intensities of boroxine and diborane, the gaseous product, were checked alternately. A rise in diborane intensity coincident with a decrease in boroxine assured that decomposition was actually occurring. Furthermore, since the instrument could be calibrated against known pressures of diborane, the initial pressure of boroxine could be calculated by quantitative comparison of corresponding changes in the two ion peaks. The expected yield of boroxine was also calculated from the stoichiometry of the B_5H_9 oxidation proposed above. Pressures of $H_3B_3O_3$ calculated by the two procedures usually agreed within 0.2 mm, thus providing a check on the stoichiometry. In subsequent runs the stoichiometric values were taken for the initial pressures of boroxine.

The rate of decomposition of boroxine was found to be highly sensitive to the amount of surface coating present (see Figure 7). In initial runs with a clean Pyrex cell the decomposition was slow, showing a zero-order dependence on boroxine pressure. In successive runs, as the white deposit containing B_2O_3 built up, the reaction rate increased and the dependence on boroxine pressure changed gradually from zero to second order. After the surface coating has become extensive, the dependence is reproducibly second order. Some typical values obtained for the rate constants were (a) in the zero-order case, $k = 0.02$ mm min^{-1} (run 1) and (b) in the second-order case, $k = 0.20$ mm^{-1} min^{-1} (run 11) and $k = 0.25$ mm^{-1} min^{-1} (run 14).

Discussion

The intensity profile for $H_3B_3O_3$ and $H_2B_2O_3$ (Figure 3) shows that while $H_3B_3O_3$ rises immediately after addition of O_2 to B_5H_9, $H_2B_2O_3$ rises rapidly only after the $H_3B_3O_3$ has reached a maximum value. This observation and subsequent results of $^{18}O_2$ labeling experiments indicate that $H_3B_3O_3$ is a precursor to $H_2B_2O_3$. In Figure 6 (I) we compare (a) observed ^{16}O–^{18}O isotopic distribution in $H_3B_3O_3$ resulting from the reaction of B_5H_9 with $^{16}O_2$–$^{18}O_2$ mixtures with those calculated with the alternative assumptions (b) that the three O atoms are distributed statistically and (c) that two atoms from a molecule of O_2 are retained by the $H_3B_3O_3$ molecule. This latter situation might arise if the immediate precursor to $H_3B_3O_3$ were a molecule with a peroxide structure. The observed distribution shows that within the uncertainties in measurement of ion intensities, the oxygen distribution in $H_3B_3O_3$ is statistical. This behavior can be explained

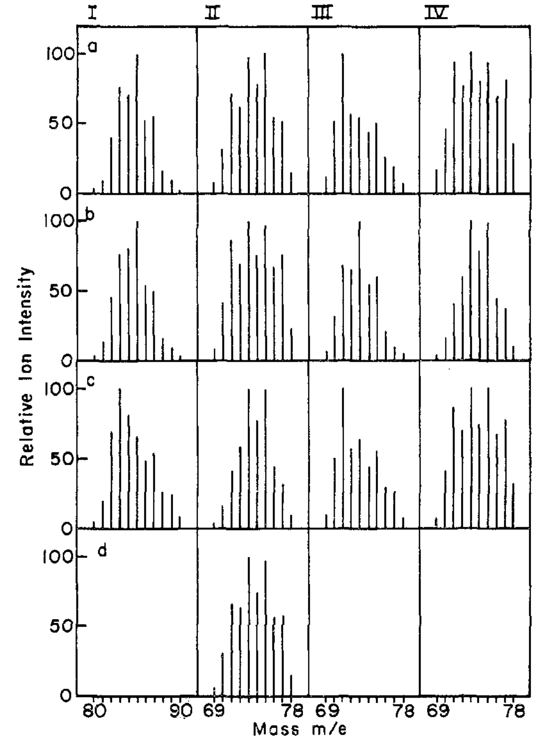

Figure 6.—I: Comparison of (a) observed mass spectrum, (b) calculated spectrum assuming statistical distribution of ^{18}O and ^{16}O, and (c) calculated spectrum assuming nonstatistical distribution of ^{18}O and ^{16}O for $H_3B_3O_3$ produced in the B_5H_9–O_2 reaction. (Ratio $^{18}O_2$:$^{16}O_2$:$^{16}O^{18}O$ = 1:1.94:0.16). II: Comparison of (a) observed mass spectrum with calculated spectra assuming (b) nonstatistical distribution of ^{18}O and ^{16}O and (c) statistical distribution of ^{18}O and ^{16}O and (d) proposed mechanism for $H_2B_2O_3$ produced in the B_5H_9–O_2 reaction. (Ratio $^{18}O_2$:$^{16}O_2$:$^{18}O^{16}O$ = 1:1:0.17.) III: Comparison of (a) observed mass spectrum with calculated spectra assuming (b) statistical distribution and (c) nonstatistical distribution of ^{18}O and ^{16}O in $H_2B_2O_3$ produced in the BH_3CO–O_2 reaction. (Ratio $^{18}O_2$:$^{16}O_2$:$^{18}O^{16}O$ = 1:1.94:0.16.) IV: Comparison of (a) observed mass spectrum with calculated spectra assuming (b) statistical distribution and (c) nonstatistical distribution of ^{18}O and ^{16}O in $H_2B_2O_3$ produced in the B_4H_{10}–O_2 reaction. (Ratio $^{18}O_2$:$^{16}O_2$:$^{18}O^{18}O$ = 1:1:0.17.)

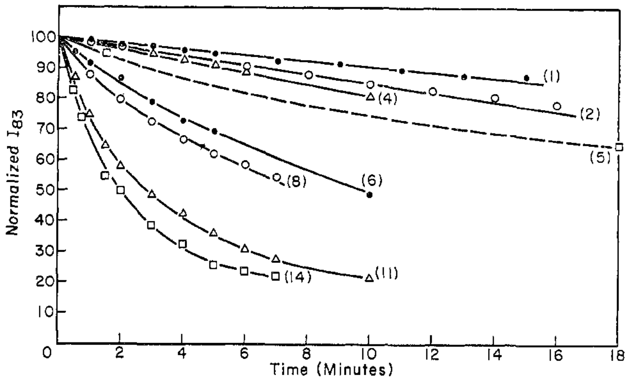

Figure 7.—Normalized ion intensity *vs.* time curves showing the effect on the decomposition of boroxine of the accumulation of solid deposits in a consecutive series of runs in the same reaction vessel. Initial boroxine pressures for the runs shown are, respectively, 1.9, 3.7, 2.7, 4.1, 1.7, 2.8, 1.9, and 2.1 mm.

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[18] W. P. Sholette and R. F. Porter, *J. Phys. Chem.*, **67**, 177 (1963).

if at some stage of the reaction the precursor to boroxine contained only one oxygen atom. Possible precursors are H_2BOH and the hypothetical HBO species. The ^{16}O–^{18}O isotope distribution in $H_2B_2O_3$ (Figure 6 (II)) is neither purely statistical nor nonstatistical as the comparison graphs indicate. This distribution can be explained by assuming that $H_2B_2O_3$ is produced by subsequent oxidation of $H_3B_3O_3$ in the stoichiometric reaction

$$H_3B_3O_3 + {}^1/_2O_2 \longrightarrow H_2B_2O_3 + {}^1/_3B_2H_6 + {}^1/_3B_2O_3 \qquad (8)$$

Earlier experiments[5] have indicated that $^{18}O_2$ "adds" to boroxine to give a molecule of $H_2B_2O_3$ containing the orginal $^{18}O_2$ molecule. Thus when a large excess of isotopically labeled O_2 is added to boroxine, the resulting $H_2B_2O_3$ should show a nonstatistical distribution typical of that shown in Figure 6 (IIb). However, for every molecule of O_2 that adds to boroxine, half of a molecule of O_2 (weighted statistically) should be regenerated. Thus when labeled oxygen is added in small increments, the $H_2B_2O_3$ should exhibit an ^{16}O–^{18}O distribution which is the sum of a nonstatistical distribution involving one molecule of oxygen and a statistical distribution involving one-half molecule of oxygen. The distribution calculated on the above assumption (Figure 6, IId) compares very closely with that observed. These observations along with ion intensity data (Figure 3) strongly indicate that $H_2B_2O_3$ is produced in this reaction by oxidation of the $H_3B_3O_3$ intermediate and not by direct oxidation of B_5H_9.

The highest yields of diborane in the B_5H_9–O_2 reaction are observed when O_2 is added very slowly. The stoichiometry curves indicate that B_2H_6 is produced in the initial stage of the reaction. Some B_2H_6 can also arise from the disproportionation of $H_3B_3O_3$,[19] but the rapid drop in boroxine results from onset of reaction 8 rather than disproportionation, since experiments on the decomposition rate of boroxine confirm that this process is slow compared with the rate of oxidation, when there is little surface coating present (as was generally the case). For example in run 1, Figure 7 (clean cell) the time required for half of the initial sample of boroxine to decompose was about 55 min. When the surface coating becomes quite extensive this time drops to the order of 2–3 min.

The zero-order dependence on the pressure of $H_3B_3O_3$ in the decomposition reaction may result when the surface sites necessary for reaction are completely occupied by adsorbed molecules. The number of adsorbed molecules of $H_3B_3O_3$ will depend on the total surface area and the competition for sites by other species in the system. As the experiment is repeated a number of times the amount of surface coating is increased. Under these conditions the reaction is more rapid and a pressure dependence on $H_3B_3O_3$ is observed. This requires that the surface reaction is fast enough to maintain a number of unoccupied sites. A plausible mechanism involves the stages

$$H_3B_3O_3(g) \rightleftarrows H_3B_3O_3(ads) \qquad (9)$$

$$2H_3B_3O_3(ads) \longrightarrow B_2H_6(g) + 2B_2O_3(s) \qquad (10)$$

To account for the second-order mechanism the rate-determining step would have to be reaction 10.

On the basis of the foregoing observations a proposed mechanism for the initial stoichiometry of the B_5H_9–O_2 reaction can be broken down into the following steps

$$B_5H_9 + O_2 \longrightarrow$$

$$3H_2BOH(ads) \longrightarrow \begin{cases} H_3B_3O_3(g) + 3H_2 & (11) \\ {}^1/_2B_2H_6 + B_2O_3(s) + 3H_2 & (12) \end{cases}$$

$$3HBO(ads) \longrightarrow \begin{cases} H_3B_3O_3(g) & \\ {}^1/_2B_2H_6(g) + B_2O_3(s) & (14) \end{cases}$$

$$(BH_2) \longrightarrow \text{diborane} + \text{borane polymer} \qquad (15)$$

Reactions 11–14 should be highly exothermic. Thermochemical data[20] indicate that the reaction to form one molecule of $H_3B_3O_3(g)$ from three molecules of $H_2BOH(g)$ is exothermic to the extent of 81 kcal/mole of $H_3B_3O_3$. In this reaction scheme the products from reactions 11–14 can be based on the consumption of 1.5 molecules of O_2 per molecule of B_5H_9. From the material balance this leaves, for each B_5H_9 molecule, a mass corresponding to the empirical composition B_2H_4.

The oxidation behavior of BH_3CO differs in several respects from that observed for B_5H_9. Mass spectral observations (*i.e.*, from monitoring *m/e* 83) indicated that boroxine was not produced when O_2 was slowly added to BH_3CO. On the other hand, $H_2B_2O_3$ is observed at the outset of this reaction (see Figure 4) and rises at a uniform rate as O_2 is added. Mass spectral patterns obtained with experiments using $^{16}O_2$–$^{18}O_2$ mixtures show that the oxygen distribution in $H_2B_2O_3$ is nonstatistical (see comparison graphs in Figure 6 (III)). This can be understood if one oxygen molecule in the reaction is retained in the $H_2B_2O_3$ structure. A possible precursor to $H_2B_2O_3$ is the hypothetical species BH_3O_2 or H_2BOOH, from which it is easy to visualize the formation of a compound containing an O–O bond as in $H_2B_2O_3$. The simplest reaction sequence which accounts for the observed over-all stoichiometry is

$$2BH_3CO + 2O_2 \longrightarrow 2BH_3O_2 + 2CO \qquad (16)$$

$$2BH_3O_2 \longrightarrow H_2B_2O_3 + H_2O + H_2 \qquad (17)$$

$${}^2/_3BH_3CO + H_2O \longrightarrow {}^1/_3B_2O_3 + {}^2/_3CO + 2H_2 \qquad (18)$$

Although H_2O was not observed, it presumably is removed immediately by further reaction with the highly reactive borane species.

Alternatively, since the over-all stoichiometry of the reaction requires less than one molecule of O_2 per BH_3CO, the presence of at least one additional precursor, possibly H_2BOH, is suggested. We can visualize as a plausible reaction sequence

$$BH_3CO + O_2 \longrightarrow BH_3O_2 + CO \qquad (19)$$

$${}^1/_3BH_3O_2 + {}^1/_3BH_3CO \longrightarrow {}^2/_3HOBH_2 + {}^1/_3CO \qquad (20)$$

$${}^2/_3BH_3O_2 + {}^2/_3HOBH_2 \longrightarrow {}^2/_3H_2B_2O_3 + {}^4/_3H_2 \qquad (21)$$

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(19) R. F. Porter and S. K. Gupta, *J. Phys. Chem.*, **68**, 280 (1964).

(20) R. F. Porter and S. K. Gupta, *ibid.*, **68**, 2732 (1964).

This would account for the over-all stoichiometry, although it cannot be ascertained whether B_2O_3 is produced in a primary reaction or by subsequent decomposition of $H_2B_2O_3$.

The most stable isomer of BH_3O_2, from the point of view of bond strengths, is $HB(OH)_2$. Calculations based on thermochemical data[5,19,20] give for the reactions

$$HB(OH)_2(g) + H_2B(OH)(g) = H_2B_2O_3(g) + 2H_2(g) \qquad (22)$$

and

$$HB(OH)_2(g) + H_2B(OH)(g) = B_2O_3(s) + 3H_2(g) \qquad (23)$$

enthalpy changes of +24 and −81 kcal, respectively. This indicates that at ordinary temperatures, only reaction 22 is thermodynamically favorable. Rearrangement of H_2BOOH to $HB(OH)_2$ should then lead to the formation of $B_2O_3(s)$ rather than $H_2B_2O_3(g)$. This type of rearrangement has been observed by Petry and Verhoek.[7a] They observed that the initial product in the gas phase reaction between $B(CH_3)_3$ and O_2, $(CH_3)_2BOOCH_3$, subsequently rearranged to form $(CH_3O)_2BCH_3$.

The mechanism of oxidation of tetraborane is very similar to that described for the BH_3CO–O_2 reaction. Boroxine is not produced in this reaction and results of experiments using oxygen enriched in $^{18}O_2$ suggest that the precursor to $H_2B_2O_3$ is formed initially without rupture of the O–O bond as in the case of the BH_3CO–O_2 reaction. Formation of BH_3O_2 is more easily visualized in the reaction of O_2 with B_4H_{10} than in the B_5H_9–O_2 reaction. Tetraborane contains two terminal BH_2 groups bridged by hydrogen atoms to the other two boron atoms. Splitting off of two BH_3 groups to form two BH_3O_2 molecules is quite feasible and this would account for the stoichiometry in reaction 7 (*i.e.*, consumption by B_4H_{10} of twice as much O_2 as in the BH_3CO case). Some evidence for this type of fission of tetraborane is given by the formation of $BH_3 \cdot py$ and $B_2H_4 \cdot py$ from tetraborane and pyridine at 0°.[21] The B_2H_4 residue can give rise to diborane and borane polymer as in the case of the B_5H_9–O_2 reaction. A similar reaction sequence corresponding to eq 16–18 can easily be written. The stoichiometry observed here of B_4H_{10} with respect to O_2 is the same as that reported by Ludlum,[22] although the over-all reaction stoichiometry is not the same.

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Notes

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The Crystal Structure of a New Polymorph of CrOOH

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Preparation of a new polymorph of chromium oxide hydroxide (CrOOH) by hydrothermal methods was reported by Tombs, Croft, Carter, and Fitzgerald;[1] the compound was identified by chemical analysis and by an X-ray diffraction powder pattern, which was indexed on an orthorhombic cell with a = 4.861 A, b = 4.292 A, and c = 2.960 A. The powder pattern of orthorhombic CrOOH is very similar to that of indium oxide hydroxide (InOOH),[2] the orthorhombic cell is comparable with the unit cell of InOOH, and the two compounds are probably isomorphous. An investigation of the crystal structure of orthorhombic CrOOH was undertaken in order to compare the two crystal structures.

Rhombohedral CrOOH[3,4] has a layer structure. Oxygen atoms are coordinated with chromium atoms in distorted octahedra. Each octahedron is sharing its six edges with six surrounding coplanar octahedra to form continuous sheets in which the oxygen atoms are close-packed. The sheets are superposed so that oxygen atoms of one sheet fall directly above those of the sheet below. The structure as a whole is therefore not close-packed and the layers are held together by short hydrogen bonds.

In structures of compounds with composition MOOH the metal atom is generally octahedrally coordinated with six oxygen atoms. In some rare earth oxide hydroxides a seven-coordination of the metal atom with oxygen atoms has been reported.[5,6] A survey of common MOOH structures has been given by Wells.[7]

A powder sample of orthorhombic CrOOH, kindly put at our disposal by the authors of ref 1, was used in the present investigation. The sample was sealed in a Lindemann glass capillary of 0.25-mm diameter. Intensities of 24 lines of the powder pattern were collected with an automatic single crystal diffractometer using Mo Kα radiation and balanced filters techniques with a scintillation counter. The diffractometer was manually operated and the intensity of each powder

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