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Oxidation of B, BH, BH_2, and B_mH_n Species: Thermochemistry and Kinetics

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Contents

Introduction 1907
Reactions of Atomic Boron 1908
Reactions of $BH(X^1\Sigma^+)$ and $BH_2(\tilde{X}^2A_1)$ 1910
Briefly: Reactions of BO 1912
The B_mH_n Species 1912
Boron-Based Fuels 1914

Introduction

For many decades interest in the high exothermicities generated during the combustion of boranes has waxed and waned. At present, preoccupation with this general problem is at a low ebb. However, while the underlying chemistry has not changed, significant sharpening of the quantitative magnitudes, derived from recent experimental and theoretical studies, is in place. Concurrently, the results of a variety of kinetic investigations provide details for developing mechanisms and thus the basis for proposing models for the oxidation processes. This review is a summary of reports published during the past four decades; it covers thermochemical and kinetic gas-phase data on the oxidation reactions of B, BH, BH_2, and B_mH_n. Parallels with analogous reactions of C(g) and CH are listed. For the radical species spectroscopic designations are included to indicate the states involved. References are cited to several more detailed compilations of data on selected aspects of the species included in this review.

It is interesting to note that while estimated magnitudes of free energy increments for reactions permit the selection of reactant combinations that have significant propensities for conversion to the indicated products, only the rates of transformation determine their practicability. Reaction rates generally correlate with derived values for the energies required to break specific bonds and are moderated by magnitudes of attractive forces between the radical species generated during the conversion sequences. Hence it is instructive first to compare diatom dissociation energies (D_0) and average bond dissociation energies (ABD) for some of the species that appear in the following discussion (Table 1). The quoted values were selected from the summary by Finch and Gardner,[1] the JANAF tables,[2] and a prepublication compilation prepared by C. F. Melius.[3] Since these sets are not entirely compatible, either mean values or those of Melius were used.

We note that only in the hydrides are ABD's larger than D_0. When a C−O bond is generated (in CO or CO_2) a higher exoergicity is developed (1075 and 803.3, respectively) than when a B−O bond is developed (in BO, BO_2, etc.). Clearly, the net effect depends on the number and types of bonds that are formed and broken during the conversion.

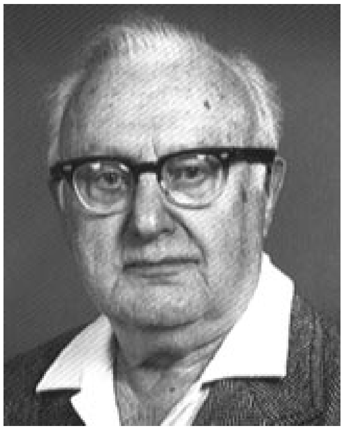

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Table 1. D_0's and Average Bond Dissociation (ABD, Energies at 300 K) (in kJ/mol)

species	D_0	species	ABD
$BH(X^1\Sigma^+)$	352.7	BH_3	373.6
$B_2(X^3\Sigma_g^-)$	290.0		
$BF(^1\Sigma^+)$	782	BF_3	644
$BCl(^1\Sigma^+)$	540	BCl_3	444
		$B{\equiv}(CH)_3$	289
		$B{\equiv}(OCH)_3$	506
		$B{\equiv}(OH)_3$	556
BO $(X^2\Sigma^+)$	808	B_2O	636
		BO_2	669
		B_2O_2	703
		B_2O_3	678

A striking feature characteristic of many boron compounds is their behavior as strong Lewis acids;

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Table 2. Specific Bond Dissociation Enthalpies (kJ/mol)

$BH(X^1\Sigma^+) \rightarrow B\ (^2P_{1/2}) + H(^2S_{1/2})$	352.7
$BH_2(\tilde{X}^2A_1) \rightarrow BH + H$	328.8
$BH_3 \rightarrow BH_2 + H$	439
$HBO \rightarrow BO(X^2\Sigma^+) + H$	460
$HBO \rightarrow O(^3P) + BH$	916

a second is the multiplicity of connectivity types that appear in boron compounds due to its participation in three-center bonds. The formation of strong H-bonds (in condensed phases) by its hydroxy-containing species is exemplified by $B(OH)_3$; its heat of sublimation is 101.7 kJ/mol. Another notable feature is the development of extended bond networks upon phase change from gaseous B_2O_3 to the liquid (heat released 417.4) and an additional 18.6 kJ/mol upon solidification. Reference to Table 2 illustrates the caveat that ABD values are representative of but are not identical with specific bond dissociations (for example, the B—H sequence).

Reactions of Atomic Boron

Elementary boron has been known since its discovery in 1807 by Davy, who electrolyzed boric acid to obtain an amorphous product. During the following century and a half other techniques were developed to prepare highly pure boron, in several polymorphic forms. However, the preparation of significant densities of the vapor is difficult since the enthalpy of sublimation is 556.5 kJ/mol. Nonetheless, reactions between atomic boron and various oxygen- and halogen-bearing species have been investigated experimentally and rate constants were derived.

The kinetics of combustion of granular boron is still not fully unraveled;[4] clearly, control of particle size distribution is a critical parameter. Reaction rates within the gas or liquid layer and on the surfaces of solid particles appear to be limited in part by the rates of diffusion of various gaseous boron and oxygen species through "liquid shells" that encase the boron granules when immersed in an oxidizing atmosphere. To facilitate the complete oxidation of boron particles suspended in hydrocarbon slurries coating the ultrafine particles with thin films of titanium or zirconium has been proposed. To be effective such coatings must have low ignition temperatures, high heats of combustion, and serve as barriers to the diffusion of oxygen into the underlying boron cores. Comixing a fluorine-bearing species also may favor more complete combustion. The homogeneous gas-phase portion of the combustion of particulate boron (with reference to liquid hydrocarbon fuels that incorporate highly dispersed granules) has been modeled by Yetter et al.[5]

Utterback and co-workers[6] generated an atomic beam of boron by laser vaporization of a thin film and crossed it with another beam of N_2O. They observed chemiluminescence and, from the dependence of its intensity on the kinetic energy of the incident boron atoms, derived relative cross sections for the reaction with nitrous oxide. Boron atoms, generated by pulsed laser ablation, reacted with ammonia during condensation with excess Ar, at 10 K.[7] The reaction products were identified via IR absorption spectra. The major primary reaction is insertion to produce an $[HBNH_2]^*$ intermediate, which dissociates to BH and NH_2.

Table 3. Maximum Exoergicities upon Formation of B—O [C—O] Bonds

$B(2s^22p,^3P_{1/2}) + OX \rightarrow BO(^2\Sigma^+) + X$

OX	X	exoergicity kJ/mol
O_3	$O_2\ (X^3\Sigma_g^-))$	−702.5
H_2O_2	H_2O	−665.7
N_2O	$N_2\ (X^1\Sigma_g^+)$	−641.8
NO_2	$NO(^2\Pi_{1/2})$	−502.5
H_2O	$H_2(^1\Sigma_g^+)$	−318.0
O_2	$O(^3P_2)$	−310.0
CO_2	$CO(^1\Sigma^+)$	−277.0
SO_2	$SO(^3\Sigma^-)$	−257.7

$C(2s^22p^2,^3P_0) + OX \rightarrow CO(X^1\Sigma^+) + X$

OX	X	exoergicity (kJ/mol)
O_3	O_2	−964.4
H_2O_2	H_2O	−1199.6
N_2O	N_2	−903.7
O_2	O	−572.4

The high exoergicities that may be anticipated when B—O bonds are generated during the abstraction of oxygen by boron atoms are compiled in Table 3, calculated under the assumption that the product oxide was produced in the lowest electronic state ($X^2\Sigma^+$). These contrast with corresponding magnitudes for similar reactions when C(g) generates CO; the latter are larger by factors 1.4—1.8.

Chen et al.,[8] using a fluorescence imaging technique, investigated the relative reactivities of the spin—orbit states in the reaction $B(^2P_{1/2};^2P_{3/2}) + O_2 \rightarrow BO(X^2\Sigma^+;A^2\Pi) + O(^3P_1)$. Their kinetic data and model calculations permitted them to detect an avoided intersection in the potential energy surfaces in the reactant valley. The product oxide species appears partitioned between the X and A states. Several interesting features of the potential energy surface were developed.

In experiments by Gole et al.[9] a beam of $B(2s^22p,^2P_{1/2})$ entered a tenuous atmosphere ($\approx 10^{-4}$ Torr) of an oxidizing gas $\{O_2, O, N_2O, NO_2, H_2O, ClO_2\}$. The emitted chemiluminescence was identified to be from $BO(A^2\Pi_{1/2})$, excited by the high exoergicies for the abstraction reaction: $B + OX \rightarrow BO^* + X$. In the emitting state, high vibrational levels were populated $\{v'\ 9$ with N_2O; $v'\ 5$ with $O_2\}$ in non-Boltzmannian distributions. They proposed that the A state gets populated both by direct reaction and by collisional energy transfer:

$$(M) + BO(X;\ \text{high } v'') \rightarrow BO(A;\ \text{low } v').$$

With H_2O, no $HBOH^*$ was observed, in contrast to the behavior of atomic aluminum which does produce $HAlO^*$.[10] The radiative lifetime of BO(A) was found to be $1.7 \pm 0.1\ \mu s$.

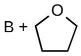
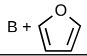
An extended series of investigations by Davidovits and co-workers[11] (over the period 1979—1988) covered reactions between atomic boron and a wide range of oxygen-bearing and halogenated compounds. They devised several ingenious techniques for preparing rough molecular beams of boron, which on entering

Table 4. Cross Sections (Å^2) for Chemiluminescence (CL), Total Reaction (TR), and k_2 [in cm^3/(mol s)] for O Atom Transfers

$$B + OY \rightarrow BO(A^2\Pi)/BO(X^2\Sigma^+) + Y$$

OY	Y	CL	TR	k_2
O_2	O	0.048	5.2	4.6×10^{-11}
SO_2	SO	0.004	13.	1.1×10^{-10}
N_2O	N_2	0.01	0.0024	2.2×10^{-14}
NO_2	NO	0.23		
H_2O_2	H_2O	0.004	5.74	(5.1×10^{-11})
CO_2	CO		0.0082	7.0×10^{-14}
H_2O	OH		0.049	4.6×10^{-12}

Table 5. Reaction Rates and Cross Sections of Boron with H_2O, H_2O_2, Alcohols, and Ethers

	k_2 [cm^3/(mol s)]	σ (Å^2)
$B + H_2O$	$(4.7 \pm 1.9) \times 10^{-12}$	0.49
$B + H_2O_2$	$(5.0 \pm 2.0) \times 10^{-11}$	5.7
$B + CH_3OH$	$(1.3 \pm 0.5) \times 10^{-10}$	15
$B + CH_3CH_2OH$	$(1.2 \pm 0.5) \times 10^{-10}$	14
$B + CH_3CH_2CH_2OH$	$(1.3 \pm 0.5) \times 10^{-10}$	16
$B + CH_3CH(CH_3)OH$	$(1.2 \pm 0.5) \times 10^{-10}$	14
$B + C(CH_3)_3OH$	$(1.2 \pm 0.5) \times 10^{-10}$	15
$B + CH_2{=}CHCH_2OH$	$(1.2 \pm 0.5) \times 10^{-10}$	15
$B + CH_3CH_2OCH_2CH_3$	$(1.4 \pm 0.6) \times 10^{-10}$	17
	$(1.2 \pm 0.4) \times 10^{-10}$	12
	$(9.8 \pm 3.9) \times 10^{-11}$	12

the collision chamber were attenuated by scattering and reaction with the oxidizer. The density of boron atoms along the beam was monitored by absorption of its resonance line (249.773 nm). Rate constants were calculated from the observed decline in boron atom density with distance from the nozzle, assuming that the abstraction reactions followed bimolecular kinetics at 300 K. Reaction cross sections were also estimated. When these investigators used a high-temperature crucible source in a modified reactor, which permitted the detection of chemiluminescence, they also demonstrated that electronically excited $BO(A^2\Pi)$ and $BO_2(\tilde{A}\Pi_u)$ were generated. The emitted radiation was spectroscopically resolved to provide data for estimating relative vibrational state populations. Their results are summarized in Tables 4−9.

It is evident that atomic boron reacts very rapidly with nearly all the oxygen- and halogen-bearing molecules, essentially at every collision. The listed cross sections may be compared to magnitudes derived from viscosity data; for relatively small molecular species these range from 10 to 14 Å^2. However, there are several reactants from which the extraction of an oxygen atom or a fluorine atom has a relatively low probability, of the order $\sim 10^{-4}$. N_2O and CO_2 are examples re BO; CF_4 and SiF_4 are examples re BF. Atomic carbon reacts with O_2 ($k_2 = 1.6 \times 10^{-11}$) slightly slower than does atomic boron,[12] but N_2O + C(g) react much more rapidly ($k_2 = 1.3 \times 10^{-11}$) than N_2O + B(g). In view of the complexity of the collision event, wherein a boron atom interacts with a complex

Table 6. Rates and Cross Sections for the Reaction of Boron with Epoxides

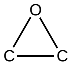
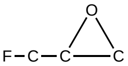
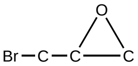
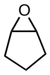
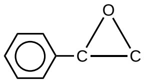
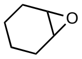
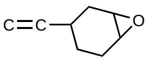
reactant	structure	k_2 [cm^3/(mol s)]	σ (Å^2)
C_2H_4O, ethylene oxide		$(3.0 \pm 1.2) \times 10^{-11}$	3.6
C_3H_5FO, epifluorohydrin		$(7.7 \pm 3.1) \times 10^{-11}$	9.5
C_3H_5BrO, epibromohydrin		$(4.1 \pm 1.6) \times 10^{-11}$	5.2
C_5H_8O, cyclopentene oxide		$(4.4 \pm 1.8) \times 10^{-11}$	5.3
C_8H_8O, styrene oxide		$(6.9 \pm 2.8) \times 10^{-11}$	8.6
$C_6H_{10}O$, cyclohexene oxide		$(4.5 \pm 1.8) \times 10^{-11}$	5.6
$C_8H_{12}O$, oxabicycloheptane		$(2.1 \pm 0.8) \times 10^{-11}$	2.7

Table 7. Rates and Cross Sections for the Reaction of Boron with the Epoxides

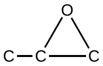
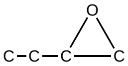
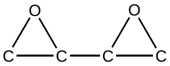
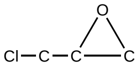
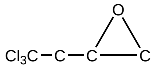
reactant	structure	k_2 [cm^3/(mol s)]	σ (Å^2)
C_3H_6O, propylene oxide		$(8.6 \pm 3.4) \times 10^{-11}$	10
C_4H_8O, epoxybutane		$(8.8 \pm 3.5) \times 10^{-11}$	11
$C_4H_6O_2$, butadiene diepoxide		$(5.5 \pm 2.2) \times 10^{-11}$	6.7
C_3H_5ClO, epichlorohydrin		$(5.7 \pm 2.3) \times 10^{-11}$	7.1
$C_3H_3Cl_3O$, 1,2-epoxy-3,3,3-trichloropropane		$(1.5 \pm 0.6) \times 10^{-11}$	1.9

Table 8. Rate Constants and Cross Sections for Boron Reactions with Halomethanes

species	k_2 [cm^3/(mol s)]	σ (Å^2)
CCl_4	$(9.5 \pm 3.8) \times 10^{-11}$	12
CCl_3H	$(4.8 \pm 1.9) \times 10^{-11}$	6.0
CCl_2H_2	$(6.2 \pm 2.5) \times 10^{-11}$	7.7
$CClH_3$	$(1.4 \pm 0.6) \times 10^{-11}$	1.7
CCl_3F	$(3.1 \pm 1.2) \times 10^{-11}$	4.0
CCl_2F_2	$(5.5 \pm 2.2) \times 10^{-12}$	0.69
$CClF_3$	$(1.7 \pm 0.7) \times 10^{-13}$	0.021
CF_4	$<3 \times 10^{-14}$	<0.003
CF_3H	$<2 \times 10^{-14}$	<0.002
CH_4	$<4 \times 10^{-15}$	<0.0004

Table 9. Rate Constants and Cross Sections for Boron Reactions with Silicon and Germanium Tetrahalides

species	k_2 [cm^3/(mol s)]	σ (Å^2)
SiF_4	$< 1.2 \times 10^{-14}$	<0.002
$SiClF_3$	$(3.2 \pm 1.1) \times 10^{-12}$	0.40
$SiCl_4$	$(8.7 \pm 3.0) \times 10^{-13}$	0.10
$SiBr_4$	$(8.5 \pm 2.9) \times 10^{-12}$	1.1
GeF_4	$(3.2 \pm 1.1) \times 10^{-11}$	4.1
$GeCl_4$	$(6.1 \pm 2.1) \times 10^{-12}$	0.81
$GeBr_4$	$(1.6 \pm 0.5) \times 10^{-10}$	21

Table 10. Exoergicities (kJ/mol) of BH and BH$_2$ Oxidations: Contrast with CH and CH$_2$

	$\Delta H(300)$
$BH + O = HBO$	-922.2
$BH + O = BO + H$	-456.5
$BH + O_2 = BO + OH$	-386.2
$BH + O_2 = HBO + O$	-419.4
$BH + O_2 = HOBO$	-971.9
$BH_2 + O_2 = BO + H_2O$	-805.4
$BH_2 + O_2 = HBO + OH$	-518.7
$BH_2 + O = HBOH$	-632.6
$BH_2 + O = BO + H_2$	-563.6
$BH + F_2 = BF + HF$	-813.4
$BH + F = BF + H$	-402.1
$BH + F = B + HF$	-216.7
$BH_2 + F = BH + HF$	-240.6
$CH + O = HCO$	-796.6
$CH + O = CO + H$	-732.6
$CH + O_2 = CO + OH$	-662.3
$CH + NO = CO + NH$	-415.1
$CH + N_2O = HCO + N_2$	-629.3
$CH_2 + O = H_2CO$	-751.4
$CH_2 + O_2 = HCO + OH$	-303.9

molecule to extract an oxygen, it is plausible to assume that such reactions involve relatively long-lived transition complexes.

Chemiluminescence was observed during B−epoxide reactions. The intensities of these emissions were measured relative to the intensities observed for B + O_2. Thereby cross sections for the production of BO(A) were estimated. These proved to be a factor $\sim 5 \times 10^{-4}$ smaller than cross sections for generating ground state BO and are therefore a measure of the probability of partitioning the net energy produced by bond formation between (translational + vibrational) vs electronic excitation. The emitted radiation was recorded with sufficient spectral resolution to permit estimation of the vibrational temperature in the A state; with propylene oxide the distribution is approximately Boltzmannian, at about 2340 K.

For silicon and germanium tetrahalides, these investigators found that MNDO calculations suggested explanations for the observed variations in cross sections. They postulated that reactions were initiated upon a shift in electron density from boron to the lowest unoccupied molecular orbital of the reacting molecule. The LUMOs of CF_4 and SiF_4 are significantly higher in energy than the LUMO of GeF_4 or the other species listed in Table 9.

When atomic boron vapor (produced by laser ablation of the solid) was codeposited with O_2 (Ar diluent) onto a salt window maintained at 11 K, IR spectra of the products indicated the presence of BO, BO_2, B_2O_2, and B_2O_3.[13] An experimental investigation of the reaction between electronically excited boron and hydrogen: $B(4p,{}^2P) + H_2 \rightarrow BH + H$ (or B + H + H) was undertaken by Yang and Dagdigian;[14] they reported rate constants for the production of excited BH($A^1\Pi$; $b^3\Sigma^-$ and $C^1\Sigma^+$), deduced from the chemiluminescence. The authors concluded that the observed products were generated through nonadiabatic transitions from highly excited BH_2 intermediates. The results of quasiclassical 3D trajectory calculations of the exoergic reaction between B(4p,^{2}P) and OH($^2\Pi$) were reported by Alberti et al.[15] They considered the effects of reagent vibrational and rotational excitation on reaction cross sections and on energy disposal in the products as well as their angular distribution. With rotational excitation, an initial decline followed by a rise in cross section was indicated. However, over the relative kinetic energy range they investigated, conversion decreased with vibrational excitation. The results appear to be quite sensitive to the shape of the assumed potential energy surface.

Reactions of BH($X^1\Sigma^+$) and BH$_2$($\tilde{X}^2A_1$)

The B/H hydrides are highly reactive radicals, characterized by corresponding high enthalpies of formation. A compilation of potential exoergicities that would be generated were they selectively oxidized in bimolecular reactions is presented in Table 10. For each of the listed combinations there are several product channels but as yet there are insufficient kinetic data to indicate the most probable reaction pathways. Comparison with similar oxidations of CH and CH_2 is instructive.

Professor C. F. Wilcox, Jr.,[16] computed the enthalpies for the sequence of intermediate products in the reactions (BH + O_2) and (CH + O_2), on their way to (BO + OH) and (CO + OH), respectively. The relative locations of the minimal energy structures are plotted in Figure 1.

Because of their high reactivities it is feasible to prepare only low concentrations of BH_n radicals; their chemical lifetimes are indeed very short. The most convenient procedure is to photolyze H_3BCO with UV radiation.[17−19] With the 193 nm line of an ArF laser BH_3, BH, and BH_2 are produced, at decreasing levels per the listed sequence. BH can be observed within 20 ns of the photolysis pulse; its concentration can be estimated by laser-induced fluorescence (LIF) from the $A^1\Pi \rightarrow X^1\Sigma^+$ transition. Radiative lifetimes and band oscillator strengths for this transition were reported by Douglass and co-workers.[20] Bimolecular rate constants at 298 K were reported by Rice et al.[21] and Harrison et al.[22] (Table 11). Recall that the corresponding kinetic binary collision rate is $\approx 8 \times 10^{-11}$.

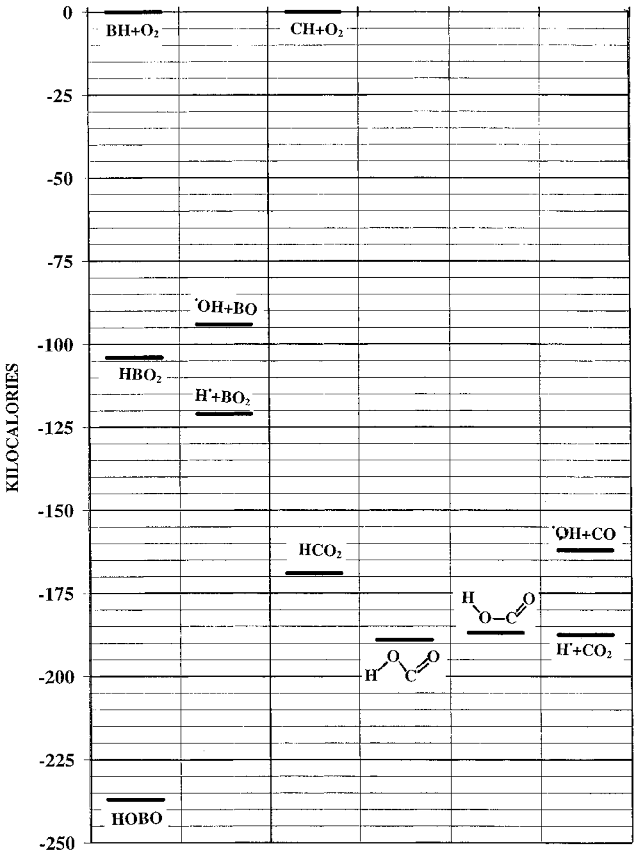


Figure 1. Computed enthalpies at 298.15 K for the various species that may be generated when O_2 adds to BH or CH. Relative to the original reactants all the products are highly exoergic.

The rate constants for loss of BH due to encounters with NO, C_2H_4, and $(CH_3)_2C{=}C(CH_3)_2$ indicate that very large attractive potentials exist between these reactants, thus enhancing their cross sections. The authors propose a set of likely pathways:

$$BH + NO \rightarrow [HBON]^* \rightarrow HBO + N$$

$$\Delta H = -286.1\ \mathrm{kJ/mol}$$

$$BH + H_2O \rightarrow [HB\cdots OH_2]^* \rightarrow HBO + H_2$$

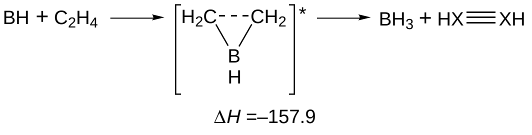
$$\Delta H = -426.8$$

$$(\text{if stabilized to } H_2BOH,\ \Delta H = -471.5)$$

$$BH + O_2 \rightarrow [HB\cdots O{-}O]^* \rightarrow HBO + O$$

$$\Delta H = -419.2$$

$$(\text{if stabilized to HOBO},\ \Delta H = -972.9)$$



$$BH + C_2H_4 \longrightarrow [H_2C{-}{-}{-}CH_2\ (B\text{–}H)]^* \longrightarrow BH_3 + HX{\equiv}XH$$

$$\Delta H = -157.9$$

Garland et al.[23] constructed a high-temperature reactor that permitted the determination of activation energies for several of the above oxidations; as anticipated these were very small. They reported

Table 11. Bimolecular Rate Constants [$cm^3/(mol\ s)$] for BH Reactions (at 300 K)

	$k_2(\pm 2\sigma)$	
reactants	ref 21	ref 22
NO	$(1.35 \pm 0.06) \times 10^{-10}$	$(1.56-6.5)\ X\ 10^{-10}$
H_2O	$(2.75 \pm 0.80) \times 10^{-12}$	
O_2	$(8.08 \pm 0.18) \times 10^{-13}$	1.1×10^{-11}
CO		1.3×10^{-13}
CO_2	$(2.64 \pm 0.15) \times 10^{-14}$	
CH_4	$<1 \times 10^{-16}$	9.4×10^{-13}
C_2H_6		1.6×10^{-12}
C_3H_8	$(7.57 \pm 0.74) \times 10^{-15}$	
C_2H_4	$(1.17 \pm 0.04) \times 10^{-10}$	$(1.3-1.7) \times 10^{-10}$
$(CH_3)_2C{=}C(CH_3)_2$	$(1.87 \pm 0.14) \times 10^{-10}$	

$$BH + O_2 \qquad k_2 = 4.9 \times 10^{-11} \exp(-1207/T)\ \mathrm{cm^3/(mol\ s)}$$

$$BH + H_2O \qquad k_2 = 5.0 \times 10^{-12} \exp(-191/T)$$

$$BH + NO \qquad k_2 = 4.5 \times 10^{-11} \exp(+241/T)$$

$$BH + D_2 \qquad k_2 = 5.8 \times 10^{-12} \exp(-1066/T)$$

The small negative activation energy exhibited in the reaction with NO indicates the initial formation of a relatively stable complex. The reaction rate constant with D_2[24] (presumably to produce HBD_2) is about one-half as large as that reported by Rice et al.[19] for the analogous association with H_2 [at 298 K, k_2 (high-pressure limit) $= 3.67 \times 10^{-13}$, compared with 1.6×10^{-13}].

Only approximate estimates, based on bond energy/bond order theory,[25] are available for the oxidation of BH by atomic halogens. With F and Cl the proposed values are $k_2\ (+F) = 3.2 \times 10^{-13} \exp(-1459/T)$ and $k_2\ (+Cl) = 2.6 \times 10^{-13}\exp(-2012/T)$.

There are no directly measured rate constants for BH_2. Estimates of its conversion rates were derived via complex mechanisms, developed for the oxidation of B_5H_9.[48] At 350 K, the following approximate bimolecular rate constants were found to fit the observed, overall reaction sequence for B_5H_9 + O:

$$BH_2 + O \rightarrow BO + H_2 \qquad k_2 = 8.3 \times 10^{-11}\ \mathrm{cm^3/(mol\ s)}$$

$$\rightarrow HBO + H \qquad k_2 = 1.7 \times 10^{-12}$$

$$\rightarrow BH + OH \qquad k_2 = 8.3 \times 10^{-14}$$

$$BH_2 + O_2 \rightarrow HBO + OH \qquad k_2 = 1.7 \times 10^{-14}$$

This section is concluded with a listing of comparative rate constants for several oxidation reactions cited for the CH radical, at 300 K and above.

$$CH + O \rightarrow CO + H \qquad k_2 = 6.59 \times 10^{-11}\ [\mathrm{cm^3/(mol\ s)}]^{26}$$

$$CH + O_2 \rightarrow CO + OH \qquad k_2 = 8.3 \times 10^{-11\ 27}$$

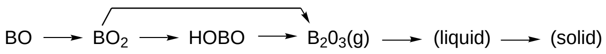
$$CH + NO \rightarrow CO + NH \qquad k_2 = 1.88 \times 10^{-10\ 28}$$

$$CH + N_2O \rightarrow CO + N_2 \qquad k_2 = 3.09 \times 10^{-11} \exp(+257/T)^{28}$$

Within an order of magnitude, these reactions take place at kinetic theory collision rates. At 300 K, {CH + NO} exchange partners 1.5−2.0 times as fast as the abstraction of an oxygen atom by BH from NO. However, {CH + O_2}, while only 0.44 as fast as with NO, is 2 orders of magnitude more rapid than abstraction of an O atom by BH from O_2. The transition structures for these oxidation reactions have not been established, but it is plausible to assume that the interaction between two Σ states {BH, $^1\Sigma^+$ + O_2, $^3\Sigma_g^-$} requires a higher activation energy than does atom transfers between reactants in Π and Σ states.

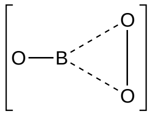
Briefly: Reactions of BO

The rates of production and reactions of BO play a central role in the complex kinetics models that have been developed[5] to account quantitatively for much of the thermo- and spectrochemical data now available for the combustion of the boranes and of their hydrocarbon derivatives. A compilation of B−O bond energies and assigned bond orders was prepared by Brown et al.[29] The following sequence of steps was postulated:



$$\begin{tikzcd}BO \arrow[r] & BO_2 \arrow[r] \arrow[rr, bend left] & HOBO \arrow[r] & B_2O_3(g) \arrow[r] & (liquid) \arrow[r] & (solid)\end{tikzcd}$$

Stanton et al.[30] generated BO by photolyzing $BCl_2(OCH_3)$ with 193 nm laser radiation and followed its local density via LIF ($A^2\Pi \rightarrow X^2\Sigma$) at 339 nm. For the reaction with O_2 they reported a bimolecular rate constant (300 → 1000): $k_2 = 7.0 \times 10^{-12} \exp(+0.26/T)$. The small negative activation energy suggested that a relatively low-energy transient adduct



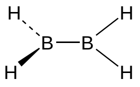
was generated on the way toward dissociation into BO_2 + O. Garland and co-workers[31] also measured the rate of the reaction between BO + H_2, which yields HBO + H. As in the above studies, they followed the decay rate of BO by LIF, but did not directly identify the products: $k_2 = (7.49 \times 10^{-23})T^{3.53} \exp(-1590/T)$. The dimer of BO is a well-established compound. It is generated when a mixture of boron and B_2O_3 is heated to ≈1475 K. Infrared spectra of matrix-isolated species and its photoelectron spectrum provide strong support for a linear configuration: O=B−B=O.[32]

It is interesting to compare the reaction {CO + OH} → {HOCO*} → {CO_2 + H} with the corresponding {BO + OH}. For the former, the recommended, overall rate constant is $k_2 = 5.40 \times 10^{-24}(T/298)^{1.5}\exp(+250/T)$.[24] As indicated, the accepted mechanism suggests the formation of a vibrationally excited complex. This was supported by several theoretical calculations.[33] For {BO + OH}, the rate constant is temperature independent ($k_2 = 4 \times 10^{-12}$),[5] whereas the production of HOBO is presumed to occur in a three-body step, with a rate constant $k_3 = 1 \times 10^{-33} \exp(+1000/T)$ and a substantial negative activation energy, as for CO.

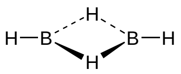
Other comparisons to note are the relative D°_{298} values for the isoelectronic pair BO and CN. The respective values are 808.8 ± 21 and 754 ± 10 kJ/mol. In contrast, for the corresponding hydrides, H−BO and H−CN, the bond dissociation energies are 460 vs 518 kJ/mol.[2b]

The B_mH_n Species

A summary of the early methods of preparation and chemical properties of the boranes was published by Hughes et al.;[34] improved syntheses were described by Shore et al.[35] The lowest member ($m = 1$; $n = 3$) is a stable molecule, but with a short lifetime because of its high reactivity either with itself, or with all Lewis bases. An initial, relatively low level QM calculation indicated that the species $m = 2$; $n = 2$ would be stable, and its global minimum structure would be linear. Recently[36] ESR data showed that the ground electronic state of HBBH is $^3\Sigma_g^-$; a higher level computation confirmed the earlier theoretical prediction. This species was prepared at 4 K by irradiating cocondensed diborane in Ne (or Ar) with UV photons. The compound $m = 2$; $n = 4$ was generated by successive abstraction of H atoms from B_2H_6 by F atoms.[37] It was detected and analyzed by photoionization mass spectrometry. Extended QM calculations[38] indicate that the two structures



and



are of comparable stability (to within 0.1 kcal/mol).

In 1975 Fehlner reviewed the then available data on the gas-phase reactions of BH_3.[39] Its propensity to dimerize ($2BH_3 = B_2H_6$) is characterized by a large enthalpy of association ($\Delta H_{ass} = -159.4$ kJ/mol), as well as by a high rate constant at 300 K: $k_2 = 6.6 \times 10^{-11}$ (estimated). For the reverse process: $k_u = 5.15 \times 10^{-12}$ s^{-1}.[40] Significant levels of BH_3 have been generated by photolysis of B_2H_6 and B_5H_9,[41] as well as of H_3BCO.[19] The latter is readily prepared by allowing diborane to equilibrate with carbon monoxide (large excess, at about 1 atm) at room temperature for several days, and separating H_3BCO by selective distillation. One may similarly prepare $H_3B{:}PF_3$. All B_mH_n compounds have Lewis acid character. Theoretical studies of adducts and oxides of boron hydrides are described in several papers.[42] $H_3B{:}X$ species, adducts of the higher boranes with bases, the B_mH_n species, and their carborane derivatives develop complex mechanisms in the process of oxidation. The high exoergicities generated during their combustion was the rationale for extensive research and development efforts devoted to the production of boron-based rocket engine fuels (see below).

The rates of association at room temperature of BH_3 with several gases were measured by Pasternack et al.[43] The borane was generated by photolysis of diborane (ArF laser, at 193 nm), comixed with the reactant species and nitrogen, as a buffer gas. The concentration of BH_3 and its decline with time were followed by its IR absorption at 1140 cm^{-1} (diode laser).

$H_3B + CO$:

$$k_2 = 1.5 \times 10^{-13} \text{ to } 47 \times 10^{-13}; \quad \text{depending on the pressure of } N_2$$

$H_3B + NO$:

$$k_2 = 3.7 \times 10^{-13};\ p(N_2) \doteq 200 \text{ Torr}$$

$H_3B + C_2H_4$:

$$k_2 = 5.2 \times 10^{-11}; \text{ no pressure dependence}$$

$H_3B + H_2O; O_2$

$$\text{too slow to be measured, } k_2 < 5 \times 10^{-15}$$

Consider now the oxidation of H_3B:X adducts [X = CO, $(CH_3)_3N$, $(C_2H_5)_3N$]. Their reaction rates with O_2, N_2O, NO, and NO_2, in a low-pressure, flow-tube reactor were too slow to be measured ($k_2 < 10^{-18}$). In contrast, with atomic oxygen and atomic nitrogen the consumption rates were very rapid.[44] In the presence of excess $O(^3P_2)$, at room temperature, the measured loss rate constants are as follows:

$H_3B{:}CO + O(^3P_2)$

$$k_2 = 6.48 \times 10^{-13} \text{ cm}^3/(\text{mol s})$$

$$H_3B{:}CO + N(^4S_{1/2}) \quad k_2 = 6.64 \times 10^{-13}$$

$H_3B{:}N(CH_3)_3$ and $H_3B{:}N(C_2H_5)_3$

$$k_2 > 2.32 \times 10^{-11}$$

For the first of the above mixtures, the following product species were detected mass spectrometrically: H_2, BO, HBO, HBOH, H_2BOH, and HOBO; BO_2 appeared only when molecular oxygen was present in the reaction zone.

To eliminate the complicating effects of O_2, a stream of N_2, diluted with He, was subjected to a microwave discharge, and the outflow was titrated with NO. This generated a stream free of O_2 and provided a measure of the oxygen atom density (equal to the measured NO consumed). When a borane was injected into this stream a bright, bluish flame developed at the tip of the injector. Strong emission from $BO(A^2\Pi)$, up to $v' = 11$ was recorded; the highest intensity appeared at $v' = 4$.[45] There was also a weak chemiluminescence from $OH(A^2\Sigma \rightarrow X^2\Pi_i)$ at 306.4 and 307.7 nm. Diffuse bands from excited BO_2 appeared in the spectral region 525−585 nm when O_2 was present. Adducts with the Lewis bases (THF, $S(CH_3)_2$, PYR, $N(CH_3)_3$, $N(C_2H_5)_3$, $N(t\text{-}Bu)_3$) gave similar results. In addition, the amine adducts generated intense emissions by CN* [$B^2\Sigma^+ \rightarrow X^2\Sigma^+$, at 358 and 388 nm] as well as lower levels of chemiluminescence from CH* at 431.4 nm [$A^2\Delta \rightarrow X^2\Pi$]. It is worth noting that the resolved BO* spectra showed a low rotational temperature (∼350 K) but high vibrational excitations, not in Boltzmannian distributions; a rough estimate indicated a vibrational temperature of ∼3000 K.

To account for the generation of the product species (listed above) and concurrently for producing a significant level of BO (in A state), it appears necessary to assume that oxygen atoms attack the boron in the adduct both from the CO side and from the H_3 side, so as to generate both BH and BH_2. One may imagine that attachment at B at CO displaces it to generate H_3BO^* ($\Delta H = -535.6$, if stabilized), which in turn dissociates either to {$H_2B + OH$} or {$HBO + H_2$}. Attacks from the H_3 end gives directly the fragments {$H_2O + BH + CO$} for which $\Delta H = -64.85$ kJ/mol. Highly energized BO can be produced via two plausible paths: $BH + O \rightarrow [HBO{:}\ ^3A' + {}^3A'']^* \rightarrow BO(A^2\Pi) + H(^2S_{1/2})$, and $BO(X^2\Sigma;\ \text{high } v'') + H$. The net ΔH available is −458.6 kJ/mol. In the presence of OH a highly exoergic reaction occurs: $BH + OH \rightarrow \{H{-}O{-}B{-}H\} \rightarrow BO(X^2\Sigma) + H_2$ ($\Delta H = -468.6$). Also, $BH_2 + O \rightarrow \{H_2BO\} \rightarrow BO + H_2$ ($\Delta H = -563.6$). The last two reactions may not produce highly excited BO because the departing H_2 could carry away considerable energy in the form of vibration and rotation.

Diborane ($m = 2$; $n = 6$) and molecular oxygen, in the absence of injected free radicals, water, or combustion catalysts do not react at room temperature, as is the case for $CH_4 + O_2$ and $C_2H_6 + O_2$. Rapid reactions are initiated when oxygen atoms are comixed with any of the three more stable hydrides (B_2H_6, B_5H_9, $B_{10}H_{14}$). At room temperature the primary initial step is an abstraction of an H atom to generate OH and a B/H radical. The time evolution of OH production, quantitated by LIF measurements at 307.9 nm {$A^2\Sigma \rightarrow X^2\Pi_i$}, for specified concentrations of $O(^3P)$ and the hydride, provide constraints on the postulated radical chains that develop.

Initial rate constants and proposed mechanisms are now available for B_2H_6,[44,46,47] B_5H_9,[48] and $B_{10}H_{14}$.[49] These data were derived from experiments in low-pressure, flow tube reactors, with He as the inert carrier gas present in large excess. Absolute values of OH concentrations were calibrated from LIF intensities produced by {$C_2H_6 + O(^3P)$}, measured under identical operating conditions as the boranes. The rate constants for the primary abstraction step and for the subsequent chain reactions for ethane are reasonably well established (see Table I, Gal and Bar-Ziv[47]}, although there are some disagreements by factors 2−3. Schematics of the complex sequences of conversions that probably take place after $O(^3P)$ atoms initiate radical production in $B_2H_6$and B_5H_9 are presented in Figures 2 and 3. Inspection of the various proposed compilations of rate constants shows that the cited values are still in a state of flux. The proposed mechanisms are not unique, due to the paucity of independently determined rate constants. From the "best set" of values, deduced by fitting the time-dependent evolution of OH concentrations for B_5H_9, rate parameters are listed in Table 12.

The data for $B_{10}H_{14}$ are fragmentary. A partial IR analysis of the hard, white solid that deposits on cold surfaces upon exit from the flow reactor indicates that its composition is $HB(OH)_2$; the presence of extended H-bonded chains B−O−H−O−B are evident.

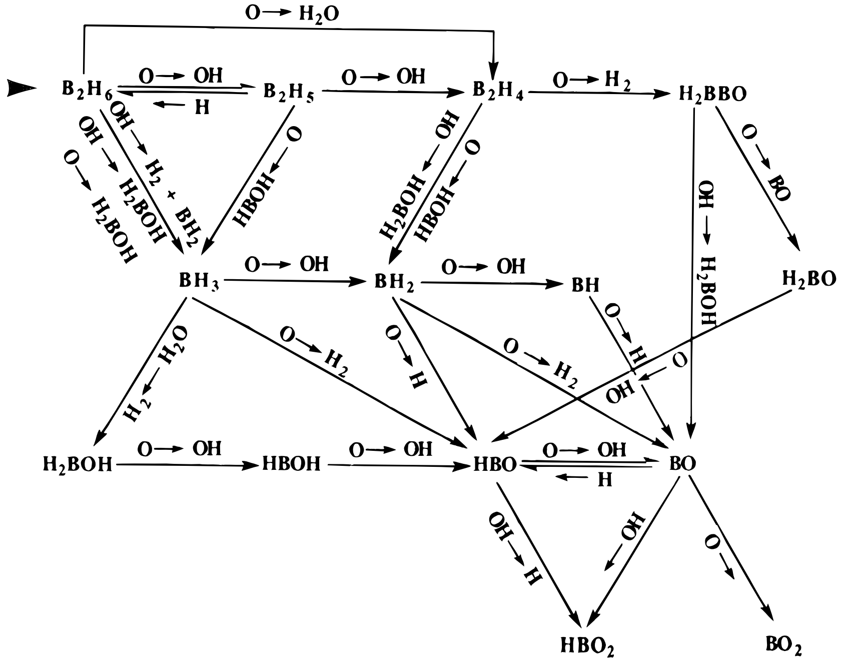


Figure 2. The complex of derivative species that appear during the oxidation of B_2H_6 via O atoms or OH radicals.

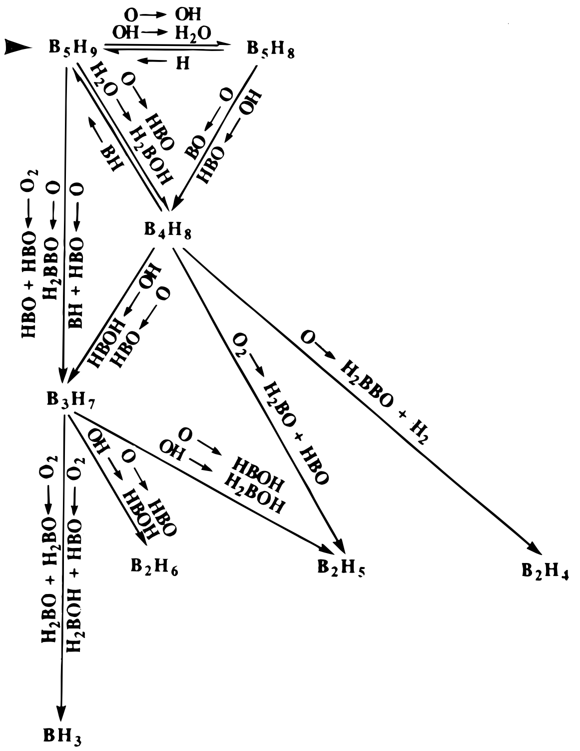


Figure 3. Additional conversions (refer to Figure 2) that are presumed to occur during the oxidation of B_5H_9.

Boron-Based Fuels

In the mid 1950s concerted efforts were devoted to pilot-scale production of boron-based fuels, justified because of their high-energy contents. The most successful of these, designated HiCal-2 ($B_5H_8C_2H_5$) and HEF-3 ($B_{10}H_{13}{\cdot}C_2H_5$) did not prove to be practical because of their high production costs and the extensive erosion induced in the engine exhausts by particulates in the combustion products.[50] There are also significant environmental limitations that arise from the toxicities of the effluents to both plants and animals. Subsequently, research efforts turned to incorporating carboranes in solid propellants for rockets,[51] where nozzle erosion is not a limiting factor. The possibility of developing B/H/N propellants was considered in the early 1960s. Were it possible to combine diborane with hydrazine under controlled conditions, to generate BN(s) and H_2, very high specific impulses would result. Various stabilized mixtures of B/H/C and N_2H_4 were tested but these did not lead to practical systems. The most recent attempts to utilize boron based-fuels were focused on developing burning-rate accelerators.[52]

In a 1963 review of the combustion of boron hydrides, W. G. Berl[53] pointed out that the early highly favorable propulsion gains anticipated for B/H fuels had to be reduced in some cases by as much as 50% because initially erroneous thermochemical data were used; in particular, the calculations did not

Table 12.

OH Production Steps for B_5H_9 at 350 °K

	k_2 [cm^3/(mol s)]
$O + HBOH = HBO + OH$	7.47×10^{-12}
$O + B_5H_9 = B_5H_8 + OH$	4.73×10^{-14}
$O + BH_3 = BH_2 + OH$	8.30×10^{-12}
$O + HBO = BO + OH$	1.66×10^{-14}
$O + H_2BOH = HBOH + OH$	6.64×10^{-12}
$O + H,(M) = (M) + OH$	1.96×10^{-14}
$O + HO_2 = O_2 + OH$	5.65×10^{-11}
$O + B_2H_6 = B_2H_5 + OH$	1.66×10^{-15}
$O + B_2H_6 = BH_3 + H_2BOH$	4.98×10^{-15}

Concurrent OH Destruction Steps

	k_2 [cm^3/(mol s)]
$OH + B_5H_9 = B_5H_8 + H_2O$	7.55×10^{-10}
$OH + O = O_2 + H$	3.82×10^{-11}
$OH + B_3H_7 = HBOH + B_2H_6$	4.90×10^{-10}
$OH + B_4H_8 = HBOH + B_3H_7$	4.90×10^{-10}
$OH + B_2H_6 = BH_3 + BH_2 + H_2O$	1.62×10^{-11}
$OH + O,(M) = HO_2 + (M)$	6.21×10^{-13}
$OH + HBO = H_2O + BO$	1.16×10^{-12}
$OH + HBO = H_2 + BO_2$	1.16×10^{-12}

include stable intermediates such as BO_2 and other stable gaseous compounds of boric oxide. He also pointed out that while it is established that such fuels burn with high flame speeds and their heat release rates are known, no convincing oxidation mechanisms within the reaction zones were available.

Among the earliest attempts to write mechanisms for the oxidation of boranes were proposals by W. H. Bauer and co-workers.[54] They found that the ultimate products of reaction of either diborane or pentaborane with O_2, under slow or explosive conditions, were B_2O_3 and H_2 (or H_2O). They argued that when $B(OH)_3$ is observed it probably was generated in a subsequent hydration of B_2O_3. Their argument has merit; once B−O−H structures are formed at any stage of the combustion they persist, and boric acid would be observed as a direct product. Limits of flame propagation in B_2H_6/C_2H_6 air mixtures were also explored, and the spectra emitted by various fuel/air flames were recorded. B_2H_6/NO mixtures burn violently, generating very high temperatures; this is a characteristic feature.

In an extensive discussion by Wolfhard, Clark, and Vanpee,[55] the authors suggest that the B_2H_6/O_2 reaction is kinetically controlled by the hydrogen reaction and that NO reacts directly with diborane rather than dissociating it prior to oxidation. They correlated burning velocities with flame temperatures for several combinations of fuels and oxidizers. The fastest in this group is B_2H_6/O_2/NO mixtures (25m/s). They concluded that the high burning velocity of diborane flames was due to fast reaction rates rather than merely to high temperatures. Also, that the principal boron-containing product in the burnt gases was HBO_2, not B_2O_3.

Somewhat later Skinner and Snyder[56] reported their shock tube studies of the pyrolysis of diborane ($520 < T < 700$ K) and measurements of induction-times for $B_2H_6/O_2/Ar$ ignition. They also investigated the effects of various additives on flame speeds in a low-pressure burner; butadiene and toluene proved most effective. With regard to the mechanism of pyrolysis, they found that the initial steps proposed by S. H. Bauer for the low-temperature regime,[57] with the addition of two steps suggested by Clapper, accounted for the decomposition over the full temperature range (360−700 K). They also explained Goldstein's observation that in the nonexplosive regime oxygen appears to retard the decomposition of diborane by scavenging the essential intermediate radical B_3H_7:

$$B_3H_7 + O_2 \rightarrow [B_3H_7O_2] \rightarrow B_3H_7O + O$$

This parallels the chain-branching step in the combustion of hydrogen. One can also account for the striking inhibition of B_2H_6/O_2 explosions at the second limit by NO_2. The similarity between B_2H_6/O_2 and H_2/O_2 flame propagation is further underscored by parallel sequences of inhibitor effectiveness.

In a subsequent communication Snyder, Zanders, and Skinner[58] described a shock tube investigation of the B_5H_9/O_2 system, over the temperature range 520−860 K. As anticipated from their B_2H_9 studies, the initial pyrolysis of B_5H_9 was shown to be independent of oxygen concentration. Butadiene, toluene, and benzene were found to be most effective in reducing flame speeds and in lengthening ignition delay times, presumably by scavenging H atoms from the preflame zone.

Table 13. Enthalpies for Reactions of B_2O_3(l) + Gaseous Reagents (Exclusive of Reactions $\Delta H° > 460$ kJ/mol)

reagent	products	$\Delta H°$ (kJ/mol)
+ O(g)	$2BO_2(g)$	453.5
+ 2O(g)	$B_2O_3(g) + O_2(g)$	−62.3
+ 2H(g)	$H_2(g) + B_2O_3(g)$	0.0
	HBO(g) + HOBO(g)	77.0
	$H_2O(g) + B_2O_2(g)$	138.1
+ OH(g)	$HOBO(g) + BO_2(g)$	387.9
+ 2OH(g)	$H_2(g) + B_2O_3(g) + O_2(g)$	358.2
	$HBO(g) + HOBO(g) + O_2(g)$	435.1
	2HOBO(g) + O(g)	321.8
	$H_2O(g) + 2BO_2(g)$	383.2
	$H_2O(g) + B_2O_3(g) + O(g)$	365.3
+ $H_2O(g)$	2HOBO(g)	392.4
+ O(g) + H(g)	$HOBO(g) + BO_2(g)$	−40.2
+ O(g) + OH(g)	$HOBO(g) + BO(g) + O_2(g)$	423.0
+ H(g) + OH(g)	$H_2(g) + B_2O_3(g) + O(g)$	428.0
	2HOBO(g)	−106.3

Both thermochemical and kinetic parameters (aside from production costs) control the potential utility of B/H/C species for specialty fuels. It is worth noting that a variety of compositions have been synthesized that have rheological properties, stabilities, ease of handling, and safety characteristics required for use as fuels. Over the past decade the enthalpies and entropies of the reactants and most of the anticipated products have been calculated and for the most part validated by direct measurements.[1−3] Also, rate constants for the key reactions are now available.[5,29,43] However, significant ambiguities still remain with regard to the distribution of products in the exhaust streams and the phase transformations that limit their ultimate exoergicities. The latter are critical. Consider the following examples: For air-breathing engines, the number of kilojoules generated per kilogram of fuel (calculated for conversions at 298 K) are B_5H_9, 6.8×10^4 (if product is B_2O_3 liq), 5.15×10^4 (if B_2O_3 is gaseous); HiCal-2, 6.07×10^4 for B_2O_3(l); $B_{10}H_{14}$, 6.55×10^4 (if product is B_2O_3 liq), 4.84×10^4 (if B_2O_3 is gaseous); HEF-3, 6.16×10^4 for B_2O_3(l).

The consequences of possible reactions between B_2O_3(l) and the ubiquitous radicals (O, H, OH) and H_2O present in the post-combustion zone that may drain enthalpy from the system are illustrated in Table 13.[59] Except for three small exoergic steps, all the others are large and endoergic.

We reach the conclusion that much interesting, indeed exciting chemistry has been developed on the basis of boron hydrides that 50 years ago were considered esoteric, unstable, and difficult to synthesize and manipulate. A wide range of novel compounds, for which B_2H_6 (or $NaBH_4$) was the starting point, found applications in synthetic organic, medicinal, and metaloorganic fields. However, their utility for augmented energy fuels remains an illusive goal.

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