

HOMOGENEOUS GAS-PHASE MODELING OF BORON/OXYGEN/HYDROGEN/CARBON COMBUSTION

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Introduction

The combustion of boron containing fuels is of importance in propulsion systems because of the potential large release of energy in going from boron to B_2O_3 . The reaction scheme



is exothermic by 467 kcal/mole. The potential energy release from boron containing fuels is considerably greater than from liquid hydrocarbon fuels and from solid fuels containing metallic aluminum. This has resulted in increased attention to fuels composed of liquid hydrocarbons with boron particles suspended in a slurry. Calculations have shown this type of fuel to be an attractive candidate for air breathing propulsion systems which are volume limited.

The calculated advantage of these fuels is based on the assumption of complete combustion to water, carbon dioxide, and liquid B_2O_3 . The combustion of boron containing fuels is a complex process involving both heterogeneous and homogeneous chemistry. First, the boron particles must be volatilized in heterogeneous processes to form gaseous boron containing species. These gas phase species then undergo homogeneous gas phase oxidation to form a mixture of boron oxide and boron oxyhydride species. The final step involves the condensation of the cooling product gases to form liquid B_2O_3 . There are two major limitations to extracting the desired performance of these fuels which have been encountered. One is that boron fuel particles are coated with B_2O_3 . This limits the initial vaporization of boron particles since B_2O_3 is difficult to remove either by vaporization or chemical reaction. The second problem is that the condensation of the final combustion products to liquid B_2O_3 may be slow, especially if boron oxyhydrides are formed as relatively long-lived intermediate species. For maximum efficiency of the combustion of boron containing fuels to be achieved, both the oxidation of the boron particles and the condensation to liquid boria must occur in the short residence time available in the system, typically less than 10^{-4} s.

Much attention has been focussed on these problems over the past several years. In this article, the homogeneous gas phase oxidation of boron, boron oxides, and boron oxyhydrides is discussed. In particular, the role of boron oxyhydrides as metastable species which contribute to the reduction of the overall combustion rate is explored. Efforts to understand this aspect of boron combustion have been hampered by the lack of basic thermodynamic and kinetic data on boron containing species. Modeling studies have been undertaken treating the gas phase oxidation step(1,2). This has helped to define some of the important species and reactions which require further study. Experimental and theoretical studies have focussed on the basic thermodynamics(3-5) and gas phase kinetics(6-10) of some of these systems. Using the results of these studies, the earlier model of homogeneous boron assisted combustion has been modified. The impact on the overall rate of combustion of these recent thermodynamic and kinetic measurements is discussed in this article. Several additional key reactions which may also have a significant impact on the model have been identified.

Model

The model used for this study is based on CHEMKIN gas-phase subroutines(11) and the SENKIN program(12) for predicting gas-phase kinetics with sensitivity analysis developed at Sandia. The modeling calculations predict the time dependence of a homogeneous gas-phase reacting mixture, based on a set of reversible or irreversible chemical reactions. As input, the code requires thermodynamic data in the form of polynomial fits to the heat capacities for all the species included in the mechanism. It also requires a list of all relevant chemical reactions, their rates, and initial species concentrations. The output of the calculation is processed using SENK PLOT graphics developed by D. Burgess of NIST.(13)

Species

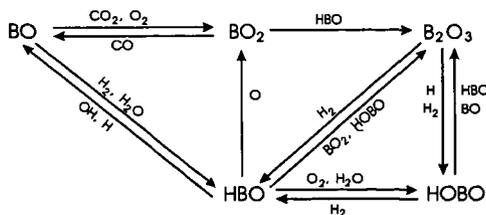
The boron-containing species used in this model include B, BO, BO₂, HBO, B₂O₂(O=B-B=O), B₂O₃(O=B-O-B=O), and HBO₂(H-O-B=O). BH, BH₂, and BOH were also included in some cases. It is assumed that in order to obtain conditions where the B₂O₃ coating on the boron particles is volatilized (T > 1800K), the hydrocarbon fuel is already oxidized. As a result, the H/O/C species used in this model include only H₂, H, O₂, O, OH, H₂O, H₂O₂, HO₂, CO, CO₂, and HCO. N₂ is included as a buffer gas, with total pressure of 1 atm.

Thermodynamics

The thermodynamic data base from Sandia(11) is augmented to include the boron compounds(14). Recently, Page(3) determined the heat of formation of HBO to be -60 kcal/mole using *ab initio* MCSCF with multireference CI techniques. This value of the heat of formation means that HBO is considerably more stable than was previously thought. The most recent JANAF recommended value for the heat of formation was -47.4 ± 3.0 kcal/mole(15). This difference has an impact on the overall boron combustion since HBO becomes a potential metastable species which could act as a bottleneck, preventing rapid combustion to B₂O₃ which is necessary for efficient energy release on the required timescale. The thermodynamic data base has been modified to include the polynomial fit to the thermodynamic properties as determined using statistical mechanics from the geometries, vibrational frequencies and heats of formation calculated by Page for HBO(3). In addition, BOH has been added to the thermodynamic data base, with the values determined in a similar manner.(5)

Kinetic Mechanism

A schematic diagram of the gas phase boron combustion pathways is shown below, which includes only the major species and the pathways which make the largest contributions to their production rates.



For our detailed kinetic mechanism, several modifications to the mechanism of Yetter, et al.(1) have been considered. All the elementary reactions included in the different mechanisms are listed in Table 1. The rates are tabulated in the form $k(\text{cm}^3\text{mol}^{-1}\text{s}^{-1}) = AT^n \exp(-E_a/RT)$. Many of the rate constants for reactions of the boron containing species are taken from reference 1. Most of these values are estimated, since only a few detailed experimental or theoretical values are available. The list of elementary reactions for the hydrogen, oxygen, and carbon species is from Yetter, Dryer, and Rabitz(16) with rates updated to reflect the more recent recommended values of Tsang and Hampson(17).

The change in the heat of formation of HBO results in several exothermic reaction pathways which were previously considered to be endothermic. In particular, the reactions of $\text{BO} + \text{H}_2 \rightarrow \text{HBO} + \text{H}$ and $\text{BO} + \text{OH} \rightarrow \text{HBO} + \text{O}$ are now calculated to be exothermic. The rate of $\text{BO} + \text{H}_2$ reaction has been measured in our laboratory and the rate of $\text{BO} + \text{OH}$ has been calculated from transition state theory. The reaction of $\text{B}_2\text{O}_2 + \text{H} \rightarrow \text{BO} + \text{HBO}$ is also calculated to be exothermic.

Reactions of B with oxidants have been measured at room temperature by DiGiuseppe and Davidovits(18,19). Oldenberg and Baughcum(20) have measured the rate of the $\text{B} + \text{O}_2$ reaction at higher temperatures. Recently, in our laboratory, rates of the reactions of BO with H_2 (6) and O_2 (7) have been measured at temperatures up to 1000K. Transition state theory has also been used to characterize the reactions of $\text{BO} + \text{H}_2$ (3,6) and $\text{BO} + \text{O}_2$ (7). These experimental rates are included in Table 1. We have also used transition state theory to characterize the reaction of $\text{BO} + \text{OH}$.

The remainder of the rate constants are estimated. The rate of reaction of $\text{B}_2\text{O}_2 + \text{H} \rightarrow \text{BO} + \text{HBO}$ is determined by comparison to other B_2O_2 reactions as estimated by Yetter, et al.(1) Several additional B and BO_2 reactions have been added, primarily to include boron hydrides in the kinetics. The rates are determined by analogy to similar reactions listed in reference 1. Reactions of BH have also been included in some of the test mechanisms. The rates of BH with O_2 and H_2O have been measured in our laboratory at temperatures up to 750K.(8) The rate of BH with CO_2 has only been measured at room temperature.(9) We assumed the same activation energy for O_2 and CO_2 reactions. The remainder of the BH reaction rates were estimated. BH_2 is not expected to play a major role in boron combustion; we have included a rate for the hydrogen abstraction from BH_2 by BO in the model which is similar in magnitude to other BO hydrogen abstraction rates.

Reactions have also been added to the mechanism to include the formation and reaction of BOH. Although this radical is not as stable as HBO, it may have a role in the combustion of boron. Rates were determined by comparison to similar reactions involving HBO and BO.

HBO reactions with O_2 and H_2O to form HBO_2 have been added. Several different rates for these reactions have been investigated in alternative mechanisms. The rates of these reactions listed in Table 1 are taken to be the same as Yetter, et al.(1) include for $\text{HBO} + \text{OH} \rightarrow \text{HBO}_2 + \text{H}$. However, the reactions of HBO with O_2 and H_2O involve more rearrangement than the substitution reaction of $\text{HBO} + \text{OH} \rightarrow \text{HBO}_2 + \text{H}$. Consequently, the rates may be slower.

Additional reactions of BO_2 abstracting hydrogen from HBO and HCO have also been included with rates analogous to the $\text{BO}_2 + \text{OH}$ and $\text{BO}_2 + \text{H}_2$ reactions which were included by Yetter, et al.(1) A competing reaction for $\text{BO}_2 + \text{HBO} \rightarrow \text{B}_2\text{O}_3 + \text{H}$ was also included.

Additional HBO_2 removal pathways by reaction with BO and HBO to form B_2O_3 have been added to the mechanism. The reaction with BO can proceed by substitution and its rate is determined by analogy to other similar substitution reactions included in the mechanism. The reaction with HBO is a four center reaction and might be expected to be slower.

Several additional oxidation pathways for $\text{B}_2\text{O}_2 \rightarrow \text{B}_2\text{O}_3$ have been added to the mechanism with rates of $6 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Their actual rates may be slower since these reactions would involve considerable rearrangement of an intermediate.

Results

Several different initial conditions have been considered in order to probe the effects of the different mechanisms and the importance of various reactions on the overall rate of boron combustion. The set of initial conditions listed in reference 2 which were derived from equilibrium calculations on a fuel rich mixture of JP4 and B(s) in air has been used. In addition, initial conditions which test the effects of all the boron being in either the form of HBO or BO have been investigated. The effects of assuming either complete hydrocarbon oxidation with H_2O and CO_2 as the hydrogen and carbon species or incomplete combustion with CO and H_2 as initial species have also been investigated.

In addition to the different initial conditions, several modifications to the mechanism which reflect the additional reactions discussed in the previous section have been studied. The first modification to the model used by Yetter, et al.(1) included the more recent thermodynamic values for HBO and the measured rates of reaction for $BO+H_2$ and $BO+O_2$. The result of these changes is to slow the overall rate of boron combustion, although the final ratio of the concentrations of the boron containing species remains similar. In addition, HBO is shown to be a potential bottleneck in the overall combustion, as can be seen in figure 1a.

This model can be modified by the inclusion of additional HBO removal processes. Adding the reactions of HBO with O_2 and H_2O increases the rate of boron combustion significantly. If the rates are on the order of $10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, HBO is no longer a metastable species slowing the boron combustion, but instead rapidly converts to HBO_2 , as shown in figure 1b. An analysis of the rate of production of HBO and sensitivity analysis of the combustion process show that these reactions are important and may in fact be controlling, especially $HBO+O_2=HBO_2+O$.

Adding BH reactions has little effect on the overall boron combustion rate since there are few effective pathways to formation of BH under these conditions. Adding reactions involving BOH has no major effect on the overall rate of combustion, although it does play a significant role in the depletion mechanism for BO. BOH is expected to be rapidly oxidized to HBO_2 .

Conclusions

The model for boron combustion has been updated to include recent experimental measurements and theoretical calculations of basic thermodynamic and kinetic data. An examination of the effects of these changes on the overall combustion rate, the production rates of the individual species, and sensitivity analysis has shown that there remain several key reactions which are in need of further study. In particular, reactions of HBO appear to be critical to the overall combustion scheme.

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Table 1. Elementary reactions included in B/O/H/C combustion mechanisms.

REACTION	A cm ³ /(mol s)	n	Ea cal/mol	REACTION	A	n	Ea
B+O2=B+O	7.24E13	0.0	310.	B0H+OH=B0+H2O	4.80E13	0.0	0.
B+OH=B+H	6.05E13	0.0	0.	B0H+O=BO+OH	4.80E13	0.0	0.
B+CO2=B+CO	3.77E10	0.0	0.	B02+H2=BH02+H	1.82E12	0.0	2980.
B+B02=2B0	3.43E13	0.0	0.	B02+OH=BH02+O	1.82E12	0.0	990.
B+O+M=B0+M	1.00E13	0.0	0.	B02+H12=BH02+H	1.82E12	0.0	990.
B+H2O=BH0+H	2.40E12	0.0	-1990.	B02+H12=H02+H	1.82E12	0.0	990.
B+HCO=BH+CO	6.03E13	0.0	2880.	B02+HCO=BH02+CO	1.82E12	0.0	990.
B+H+M=BH+M	1.00E15	0.0	0.	B02+H+M=BH02+M	1.82E12	0.0	-1990.
B+H2=M+BH2+M	1.10E11	0.0	-1990.	B02+HCO=B2O3+H	6.03E10	0.0	9940.
B+H2O=BOH+H	4.80E12	0.0	0.	B02+OH=B2O3+H2O	1.82E12	0.0	990.
B+OH=M+BOH+M	1.10E15	0.0	0.	H02+BO=B2O3+H	4.80E12	0.0	1990.
BH+O2=BH0+O	3.00E13	0.0	-1990.	H02+H=H0+H	4.80E12	0.0	0.
BH+H2O=BH0+H2	3.00E12	0.0	2400.	B2O3+H=BOH+BO	3.43E13	0.0	0.
BH+CO2=BH0+CO	9.00E11	0.0	2400.	B2O3+H=BOH+BO	3.43E13	0.0	0.
BH+O+M=BH0+M	1.10E15	0.0	-1990.	B2O3+OH=BOH+BO2	3.43E13	0.0	0.
BH+OH=BH0+H	3.00E13	0.0	2400.	B2O3+OH=B0+BH02	3.43E13	0.0	0.
BH+B02=BH0+B0	9.00E11	0.0	2400.	B2O3+OH=B02+HBO	6.03E8	0.0	69940.
BH+BO=BH0+B	3.00E12	0.0	2400.	B2O3+O2=2B02	6.03E8	0.0	80080.
BH+B02=2BH0	9.00E11	0.0	380.	B2O3+O2=2B02+H	6.03E11	0.0	0.
BH2+B0=BH0+BH	6.03E11	0.0	2400.	B2O3+CO2=B2O3+CO	6.03E11	0.0	0.
HBO+OH=B0+H2O	4.79E13	0.0	0.	B2O3+OH=B02+BO	6.03E11	0.0	0.
HBO+O=BO2+H	6.03E3	0.0	70000.	B2O3+OH=B02+BO2	6.03E8	0.0	11920.
HBO+OH=B02+H	4.79E12	0.0	0.	HCO+H=CO+H2	1.21E14	0.0	0.
HBO+O2=B02+O	4.79E12	0.0	0.	HCO+O=CO+OH	3.01E13	0.0	0.
HBO+H2O=BH02+H	4.79E12	0.0	0.	HCO+O2=H02+CO	5.12E13	0.0	1690.
HBO+OH=BH02+H	4.79E12	0.0	0.	H02+CO=CO2+OH	1.51E14	0.0	23650.
HBO+O+M=BH02+M	3.63E20	-0.5	50070.	CO+OH=CO2+H	4.39E6	1.5	-740.
B0+O2=B02+O	4.21E12	0.0	-507.	CO2+O=CO+O2	1.69E13	0.0	52660.
B0+OH=B02+H	2.40E12	0.0	0.	H+O2=OH+O	1.20E17	-0.91	16520.
B0+O+M=B02+M	1.10E15	0.0	-1990.	O+H2=OH+H	5.06E4	2.67	6290.
B0+CO2=B02+CO	6.03E10	0.0	9940.	O+H2O=2OH	4.58E9	1.3	17100.
B0+CO=B02+CO	4.21E12	0.0	-507.	H+H2O=OH+H2	6.19E7	1.9	18410.
B0+OH=BH02+H	3.43E14	0.0	9940.	O+H02=O2+OH	1.75E12	0.0	320.
B0+OH+M=BH02+M	4.32E01	3.53	3160.	H+H02=O2+H	1.69E14	0.0	-400.
B0+H2=B0H+H	4.32E01	3.53	3160.	H+H02=H2+O2	6.62E13	0.0	2130.
B0+H2+M=B0H+M	1.64E05	2.76	5015.	O+H02=H2+O	1.45E16	-1.0	39740.
B0+H2O=B0H+H	7.92E13	0.0	-1990.	OH+H02=H2O+O2	5.42E13	0.0	26030.
B0+B02=B0+B0	4.20E12	0.0	-507.	H02+O2=2H02	3.01E13	0.0	118100.
B0H+B02=B0H+B0	4.20E12	0.0	-507.	O2+H+O+H	1.81E18	-1.00	96000.
B0H+CO2=BH02+CO	4.20E12	0.0	-507.	O2+H+OH+H	2.20E14	0.0	96000.
B0H+OH=BH02+H	2.40E15	0.0	990.	O2+O+OH+H	2.41E15	0.0	99360.
B0H+H2O=BH02+H2	6.00E10	0.0	9940.	H2O+H+OH+H	1.29E33	-4.86	53250.
B0H+O+M=BH02+M	1.10E15	0.0	-1990.	H2O+H+OH+H	3.49E15	0.0	109120.
B0H+CO=B02+H	4.80E13	0.0	0.	H2O+H+OH+H	3.21E13	-1.18	48410.
B0H+H2O2=B0H+H2O	4.80E13	0.0	0.	HCO+H+CO+H	5.11E21	-2.14	20420.
B0H+H2O2=2B0H	4.80E13	0.0	0.	H+H2O2=H2O+OH	2.41E13	0.0	3970.

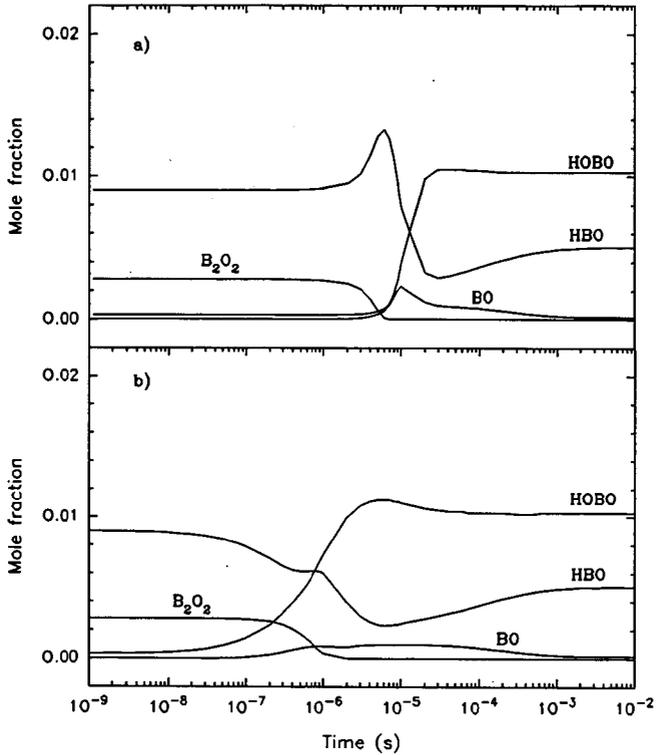


Figure 1. Species profiles as a function of time for an adiabatic, constant pressure (1atm) system. The initial species mole fractions, derived from the equilibrium gas phase calculations of reference 2, are as follows: $X(\text{HBO})=9 \times 10^{-3}$, $X(\text{B}_2\text{O}_2)=2.8 \times 10^{-3}$, $X(\text{B}_2\text{O}_3)=5 \times 10^{-4}$, $X(\text{HBO}_2)=3 \times 10^{-4}$, $X(\text{O}_2)=4.4 \times 10^{-2}$, $X(\text{CO})=0.18$, $X(\text{H}_2)=0.20$, $X(\text{H})=1 \times 10^{-4}$, $X(\text{H}_2\text{O})=1 \times 10^{-5}$, and $X(\text{N}_2)=0.56$, with an initial temperature of 1800K. a) The mechanism includes the more recent thermodynamic value for the heat of formation of HBO and the measured rates of reaction for $\text{BO}+\text{H}_2$ and $\text{BO}+\text{O}_2$, as described in the text. b) Additional HBO removal processes are added to the mechanism.