REACTION CHEMISTRY OF BORON HYDRIDES

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We have recently begun a program on Boron Combustion Chemistry in the Chemistry Division at NRL. Our initial efforts have involved investigations of the room temperature reactions of BH\(_3\)\(^1\) and BH\(_2\)\(^2\) with various oxidants and hydrocarbons. In conjunction with the gas-phase experimental work, we are pursuing a computational study of the heats of formation of boron compounds and reaction energetics. In addition, there is a compound of the program emphasizing the heterogeneous chemistry of boron oxides.
We have recently begun a program on Boron Combustion Chemistry in the Chemistry Division at NRL. Our initial efforts have involved investigations of the room temperature reactions of BH₃ [1] and BH [2] with various oxidants and hydrocarbons. In conjunction with the gas-phase experimental work, we are pursuing a computational study of the heats of formation of boron compounds and reaction energetics. In addition, there is a component of the program emphasizing the heterogeneous chemistry of boron oxides.

BH₃ is produced by the 193 nm photolysis of BH₃CO or B₂H₆. BH is only observed after BH₃CO photolysis, not from B₂H₆. BH₃ is probed by monitoring time resolved IR absorption in the Q-branch of the ν₂ band near 1140 cm⁻¹ using a tunable diode laser. Most experiments were performed with B₂H₆ as the photolytic precursor because of less spectral congestion in the IR. A schematic diagram of the apparatus used for BH₃ measurements is shown in Figure 1. The BH experiments are carried out in a more conventional laser photolysis/laser induced fluorescence apparatus in which BH is probed by exciting fluorescence in the A¹Π ← X¹Σ⁺ system near 430 nm.

We find the association reaction of BH₃ with CO to be in the intermediate pressure regime over the pressure range studied (10-620 Torr, N₂) with rate constants ranging from 1.5 to 47 x 10⁻¹³ cm³ s⁻¹. For BH₃ + NO, the rate constant approaches the high-pressure limit of 3.7 x 10⁻¹³ cm³ s⁻¹ at pressure ≥ 200 Torr N₂. The pressure-independent rate constant (P ≥ 6 Torr) for the reaction of BH₃ with C₂H₄ is (5.2 ± 1.0) x 10⁻¹¹ cm³ s⁻¹. For the reactions BH₃ with O₂ and H₂O we are able to place upper limits of 5 x 10⁻¹⁵ and 6 x 10⁻¹⁵ cm³ s⁻¹, respectively, on the reaction rate constants.

Room temperature reactions of BH are primarily pressure-independent in the 5 to 1000 Torr pressure range. The rate constants derived from our measurements are listed in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k (cm³ s⁻¹)</th>
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<tbody>
<tr>
<td>BH + NO</td>
<td>(1.35 ± 0.03) x 10⁻¹⁰</td>
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<tr>
<td>BH + H₂O</td>
<td>(9.76 ± 0.40) x 10⁻¹²</td>
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<tr>
<td>BH + O₂</td>
<td>(8.08 ± 0.09) x 10⁻¹³</td>
</tr>
<tr>
<td>BH + CO₂</td>
<td>(2.64 ± 0.07) x 10⁻¹⁴</td>
</tr>
<tr>
<td>BH + C₂H₄</td>
<td>(1.17 ± 0.02) x 10⁻¹⁰</td>
</tr>
<tr>
<td>BH + TME⁻</td>
<td>(1.87 ± 0.07) x 10⁻¹⁰</td>
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</table>

a) 2,3 dimethyl-2-butene
We have also studied the reaction of BH with H2 and are able to measure the pressure dependence of this reaction over the range 10-700 Torr (see Figure 2) and extract the following kinetic parameters: \( k_0 = (1.05 \pm 0.11) \times 10^{-31} \text{ cm}^6 \text{ s}^{-1} \), \( k_\infty = (3.52 \pm 0.42) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \), and \( F_c = 0.51 \pm 0.06 \). The reaction of BH with CO is in the transition region at these pressures with the rate constant ranging from 3.9 to 58 \( \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \).

Mechanistic details inferred from these measurements and our plans for further work in this field will be discussed.

References:


Figure 1. Schematic diagram of the apparatus used to study BH3 reactions.
Figure 2. Observed pressure dependence for the reaction BH + H$_2$ at room temperature. The solid line is a fit to the data using parameters given in the text. The dashed line is the fitted high pressure limit.