Gas-Phase Detection of the HBCC ($X^1\Sigma$) Molecule: A Combined Crossed Beam and Computational Study of the $B(^2P) + C_2H_2(^1\Sigma_g{}^+)$ Reaction

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Dedicated to Professor Paul von R. Schleyer

ABSTRACT: A novel supersonic beam of ground-state boron atoms [$B(^2P)$] was employed to investigate the reaction of $B(^2P)$ with acetylene [$C_2H_2(^1\Sigma_g{}^+)$] at an average collision energy of 16.3 ± 0.4 kJ mol^{-1} at the most fundamental microscopic level. The crossed molecular beam technique was used to record time of flight spectra at mass to charge ratios of 36 ($^{11}BC_2H^+$), 35 ($^{10}BC_2H^+/^{11}BC_2{}^+$), and 34 ($^{10}BC_2{}^+$) at different laboratory angles. Forward-convolution fitting of the laboratory data showed that only a product with the gross formula BC_2H was formed via a boron versus hydrogen exchange. By combining experimental results with electronic structure calculations, the conclusion was that the reaction proceeded via the initial addition of $B(^2P)$ to the two carbon atoms of acetylene, leading to the formation of a first intermediate, the borirene radical (c-BC_2H_2). This intermediate underwent various isomerization processes on the BC_2H_2

potential energy surface before decomposing into the linear $HBCC(X^1\Sigma)$ isomer via a hydrogen atom elimination.   © 2001 John Wiley & Sons, Inc.   J Comput Chem 22: 1359–1365, 2001

Introduction

The crossed molecular beam (CMB) method with mass spectrometric detection is well established as a powerful tool to unravel the mechanism of reactions that form polyatomic products, the spectroscopy of which is not known and is hence not accessible to optical detection schemes, such as laser induced fluorescence.[1, 2] Even though CMB experiments are now available on the reactions of most of the light atoms of the periodic table, an experimental investigation on the reaction dynamics of boron atoms has not been performed. The present knowledge of ground-state (^2P) atomic boron reactions is primarily based on kinetic measurements monitoring the decay of the boron concentration[3] and matrix studies of atomic boron reacting with O_2, H_2O, N_2, CO, HCN, NH_3, H_2, and hydrocarbons (CH_4, C_2H_2, C_2H_4, and C_2H_6).[4, 5] However, these investigations can only speculate on the inherent reaction mechanism(s), because the effects of matrix trapping, the composition of the beam, and the poorly defined energy of the boron reagent do not allow a definite assignment of the elementary steps of the mechanism that are involved. Therefore, new systematic studies of these important reactions under well-defined experimental conditions are needed to understand the chemical behavior of this atomic species.

Thus far, the reaction mechanism was investigated only for the reaction of electronically excited boron [B(^2D)] with molecular hydrogen via excitation of a B–H_2 van der Waals complex; the formation of atomic hydrogen and electronically excited boron monohydride (BH) in the $A^1\Pi$ and $a^3\Pi$ states[6] was observed. This system is a prototype for the reactions of electronically excited boron atoms, but the reaction mechanism of the ground-state atomic boron was expected to be different.

In the reaction with unsaturated hydrocarbons the addition to the π system was expected to be dominant, because atomic boron is strongly electrophilic; this was actually observed in the first CMB study of the ground-state atomic boron reaction, which elucidated the reaction mechanism of the B(^2P) + $C_2H_4(^1A_g^+)$ reaction.[7] Matrix studies by Andrews and coworkers also suggested an additional pathway proceeding through insertion of boron atoms into C—H bonds.[5]

In this article we focus on the B(^2P) + $C_2H_2(^1\Sigma_g^+)$ reaction studied under single collision conditions as provided in crossed beam experiments. These detailed insights into the reaction dynamics allowed us to characterize the pathways leading to BC_2H-isomers. We also performed a high level computational study to characterize the relevant stationary points along the BC_2H_2 potential energy surface (PES).

Besides its fundamental interest, the title reaction also has some practical implications; for instance, no organo-boron molecule has been detected in extraterrestrial environments so far. The results of our studies provide a clue to the boron-bearing organic molecule that must be searched in the interstellar medium or in circumstellar envelopes.

Experiment and Data Processing

The experiments were performed with a 35″ CMB apparatus described in detail in a previous study.[8] The atomic boron beam was produced by using the same ablation source that was successful in generating the carbon atom and cyano radicals beams.[9] Briefly, a pulsed supersonic boron beam was generated via laser ablation of boron at 266 nm. The 30 Hz, 35–40 mJ output of a Spectra Physics GCR 270-30 Nd-YAG laser was focused onto a rotating boron rod, and ablated atoms were subsequently seeded into helium gas released by a Proch–Trickl pulsed valve. No boron clusters were present; the intensities of the integrated time of flight (TOF) spectra at mass to charge ratios (m/e) of 10 (^{10}B) and 11 (^{11}B) reflected the natural isotopic abundance ratio of 80% ^{11}B versus 20% ^{10}B. A chopper wheel mounted after the laser ablation zone selected a 9-μs segment of the pulse of a peak velocity (v_p) of 1846 ± 5 ms^{-1} and a speed ratio (S) of 7.9 ± 0.1. This pulse crossed a pulsed acetylene beam ($v_p = 900 \pm 10$ ms^{-1}, $S = 9.0 \pm 0.1$) perpendicularly at an averaged collision energy of 16.3 ± 0.4 kJ mol^{-1} in the

interaction region. The scattered species were monitored via TOF spectra using a triply differentially pumped UHV ($<8 \times 10^{-13}$ mbar) detector consisting of a Brink-type electron impact ionizer, a quadrupole mass filter, and a Daly ion detector.

Information on the reaction dynamics was extracted from the TOF spectra and the laboratory angular distribution (LAB) by using a forward-convolution technique. This iterative approach initially guesses the angular flux distribution in the center of mass (CM) coordinate system [$T(\theta)$] and the translational energy flux distribution in the CM system [$P(E_T)$], which are assumed to be independent of each other. The final outcome is the generation of a velocity flux contour map $I(\theta, u) \sim P(u) \times T(\theta)$ in the CM frame showing the intensity as a function of angle θ and velocity u. This map serves as an image of the title reaction and contains the basic information of the scattering process.

Computational Study

The stationary points on the BC$_2$H$_2$ PES were first located at the B3LYP/cc-pVDZ level of theory.[10, 11] The harmonic frequencies were calculated at the same level to characterize the stationary points [minima vs. the transition state (TS)] to obtain zero-point vibrational energy (ZPVE) and to generate force constant data needed in the intrinsic reaction coordinate (IRC) calculations.[12] The IRC calculations were performed at the B3LYP/cc-pVDZ level to check that the TSs connected the presumed minima. Total energies were refined at the CCSD(T)/cc-pVTZ level[13] using B3LYP/cc-pVDZ optimized geometries with B3LYP/cc-pVDZ ZPVE corrections. All calculations were conducted with Gaussian 94.[14]

Experimental Results

The reactive scattering signal was observed at m/e of 36 (^{11}BC$_2$H$^+$) (Figs. 1, 2), 35 (^{10}BC$_2$H$^+$/^{11}BC$_2^+$), and 34 (^{10}BC$_2^+$). The TOF spectra at m/e values of 35 and 34 could be fit with the same CM functions, revealing that only a molecule with the gross formula BC$_2$H was formed via a boron atom versus hydrogen replacement channel. Mass to charge ratios higher than 36 were not observed.

The LAB distribution of the BC$_2$H product(s) as shown in Figure 2 peaked at the CM angle of $49.0 \pm 1.0°$. This distribution had a slight asymmet-
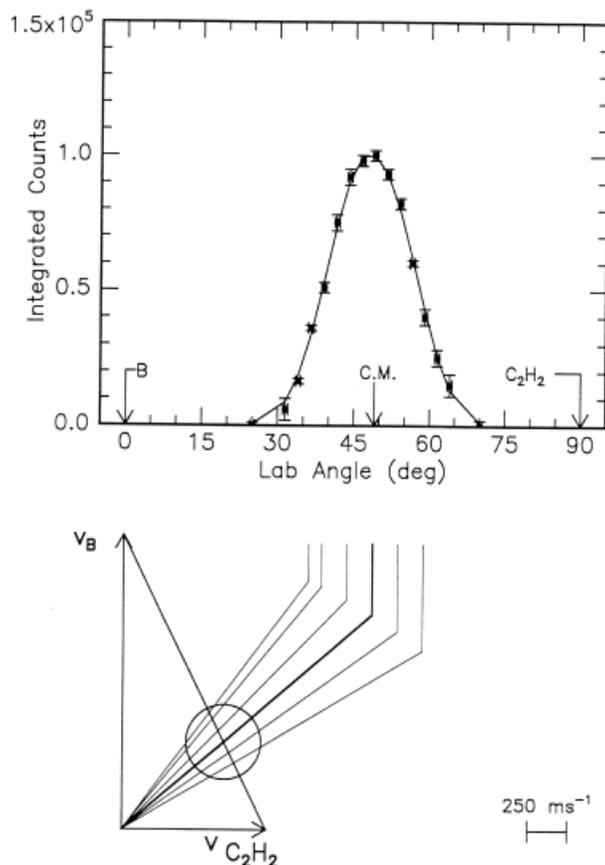

FIGURE 1. (a) The laboratory angular distribution of the product channel at $m/e = 36$. The error bars indicate experimental data; (—) the calculated distribution.
(b) The Newton diagram for the B(^{2}P) + C$_2$H$_2$($^1\Sigma_g^+$) reaction. The circle is the maximum center of mass recoil velocity of the BCCH product.

ric shape, depicted a higher intensity at angles close to the boron beam, and was very broad and extended 40° in the scattering plane defined by the boron and acetylene beams. This suggested that a significant amount of the total available energy was released into translation of the reaction products. In addition, the $P(E_T)$, and hence the velocity flux contour (Fig. 3) map, should have a maximum away from zero as it was actually found at 10–15 kJ mol^{-1}. In our experiments the best fit of the LAB distribution and TOF spectra was achieved with $P(E_T)$s extending to 35–60 kJ mol^{-1}. If we accounted for the collision energy of 16.3 kJ mol^{-1}, the title reaction was found to be exothermic by 19–41 kJ mol^{-1}.

The angular part of the contour plot was useful to extract additional information on the chemical reaction dynamics. This plot showed intensity in
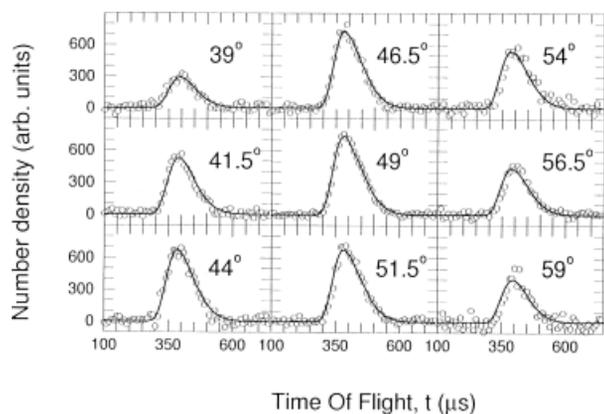
FIGURE 2. The time of flight data for selected laboratory angles at $m/e = 36$.

the full angular range from 0 to 180°, suggesting the formation of a BC_2H_2 complex(es). Also, the contour map was slightly forward scattered with respect to the boron beam, suggesting that either an osculating complex holding a lifetime comparable to its rotational period was formed or two distinct microchannels were active. The weak polarization was the result of poor coupling between the initial (L) and final orbital angular momentum (L'), indicating that most of the total angular momentum channeled into rotational excitation of the BC_2H product. In addition, the B and the leaving hydrogen atom must be located on opposite sites of the rotation axis to account for the forward scattering of BC_2H.
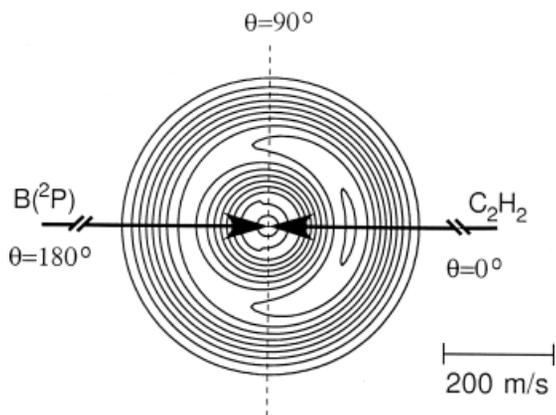

FIGURE 3. The velocity flux contour map in the center of mass reference frame for the reaction $B(^2P) + C_2H_2(^1\Sigma_g^+) \rightarrow BC_2H + H$. The contour lines connect data points with an identical flux.

Computational Results

Our *ab initio* calculations showed that, in agreement with a previous study, the linear HBCC ($X^1\Sigma$) isomer (**6**) was the global minimum on the BC_2H PES (cf. Fig. 4).[5] The overall reaction was exothermic by 6.9 kJ mol^{-1} at the CCSD(T)/cc-pVTZ ZPVE level; G2 data yielded an exothermicity of about 18 kJ mol^{-1} closer to the experimentally derived value. The next most stable isomer was the linear HCCB molecule in its $^1\Sigma$ ground state (**7**). Because the reaction of $B + C_2H_2$ to HCCB plus atomic hydrogen was predicted to be endothermic by 24.7 kJ mol^{-1} (19.2 kJ mol^{-1} at the G2 level), but our collision energy was only 16.7 kJ mol^{-1}, only HBCC was energetically accessible. Other HC_2B isomers were even higher in energy and are the subject of a forthcoming publication.[15] Therefore, we focused on the channels leading to the HBCC isomer. Two entrance channels were located via addition of $B(^2P)$ to one carbon of acetylene forming *trans*-BCHCH (X^2A', **1**)[16] or to both carbon atoms yielding the aromatic borirene radical c-BC_2H_2 (X^2A_1, **2**). The first channel leading to **1** had a large entrance barrier (50.5 kJ mol^{-1}) and therefore would not contribute to the reaction at our collision energy. The second entrance channel was without a barrier. Some comments need to be made because **2** does not correlate in C_{2v} with the reactant ground states. However, there was a π complex (X^2B_2) that correlated with the reactants. Going from a C_{2v} to C_s approach of the B atom to acetylene, the symmetry was reduced to $^2A'$, which would have avoided crossing with **2** as pointed out by Flores and Largo.[17] This was consistent with the matrix isolation experiment of Andrews et al. in which the absorption bands of the borirene radical grew with annealing above 18 K, leading to the conclusion that **2** was produced by the reaction of cold boron atoms with C_2H_2.[5] The borirene radical can rearrange through **2**′ via a H shift to **4**; **2**′ can be best described as a H-bridged hydrogen-deficient carbon-bearing borane species that is only metastable and rearranges rapidly to **4**. The latter represented the global minimum of the BC_2H_2 PES and was stabilized by 312.4 kJ mol^{-1} with respect to the separated reactants. The **4** compound can either ring open to **3** or **5** and/or lose a hydrogen atom to form the HBCC product via an exit barrier of 12.6 kJ mol^{-1}. In addition, **3** and **5** can emit a hydrogen atom without a barrier to yield **6**. The geometry of **3** at the B3LYP level was very close to the one obtained in Andrews et al.[5] at the QCISD level of theory: only the B—C length
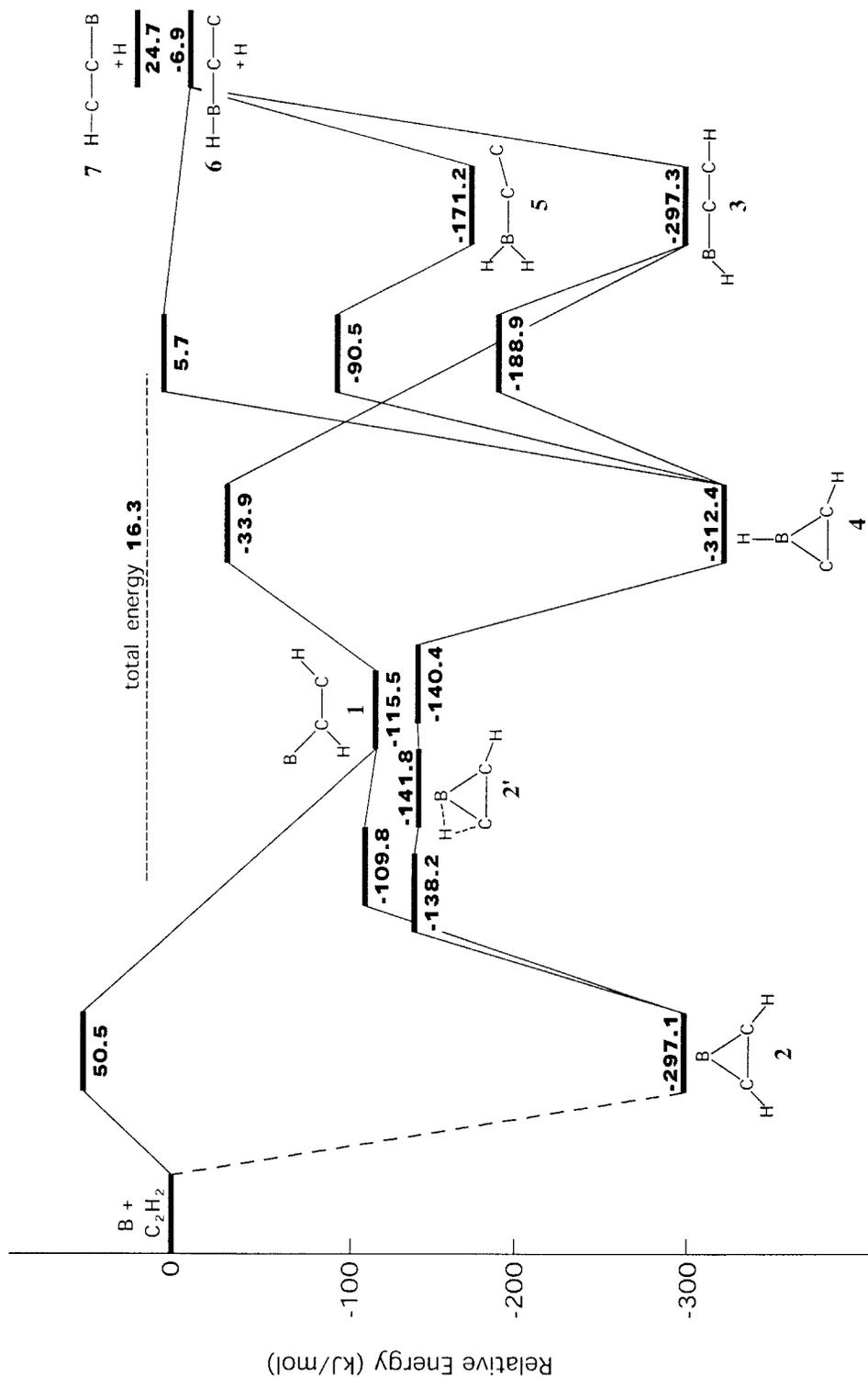
FIGURE 4. The potential energy surface for the reaction of B(^{2}P) with C$_2$H$_2$($^1\Sigma_g^+$). The reported relative energies were obtained at the CCSD(T)/cc-pVTZ//B3LYP/cc-pVDZ level with B3LYP/cc-pVDZ ZPVE corrections. Only those pathways leading to the HBCC isomer are shown. The transition state (TS) X/Y in the text denotes the transition structure connecting X and Y minima. The bond orders are not indicated on the schematic structures of the minima and products.

was found to be 0.03 Å shorter, tests were performed to investigate the energetics of this species (CCSD(T)/cc-pVTZ) at geometries obtained at the B3LYP/cc-pVDZ and QCISD/cc-pVDZ levels, and the values were virtually equal.

Discussion

If we combine our experimental and theoretical results, the following chemical reaction dynamics are likely. First, the solid identification of the boron versus hydrogen exchange pathway together with the calculated reaction energies clearly identify the linear HBCC isomer in its $^1\Sigma$ electronic ground state as the only reaction product. The experimentally derived reaction exothermicity lies closer to the theoretical G2 data. Second, the reaction proceeds via the initial addition of B(^{2}P) to two carbon atoms to the c-BC$_2$H$_2$ (**2**) intermediate, which undergoes H atom migration to **4**. Because of an optimum orbital overlap, the initial collision complex **2** likely rotates around the B axis, which in turn is parallel to the total angular momentum vector **J**.

The cyclic isomer (**4**) was identified as the most important reaction intermediate. This complex can fragment via atomic hydrogen loss to the HBCC product in its electronic ground state. Due to angular momentum conservation, this linear isomer must be rotationally excited to B-like rotations as demonstrated by a weakly polarized contour plot. Likewise, the leaving hydrogen and incorporated B atom were on opposite sites of the B rotation axes and hence could account for the observed forward scattering. Further, **4** isomerized to **3** prior to a barrierless decomposition of this intermediate to atomic hydrogen and the HBCC isomer. Because of the larger barrier of TS **4–5** compared to TS **3–4**, we anticipated that isomer **5** played only a minor role in the reaction, if any. Finally, **4** can decompose via a tight exit TS to HBCC. This was verified experimentally as the translational energy distribution peaks well away from zero translational energy. Only a decomposing intermediate (**3**) was expected to result in a $P(E_T)$ peaking at zero energy that was attributable to the absence of any exit barrier.

At the present stage, we cannot assign the relative contributions of **3** and **4** in decomposing to HBCC (**6**). Thus, we must investigate further if the observed forward peaking is the result of an osculating complex or the effect of two microchannels with distinct scattering dynamics as found in the C(^{3}P)/C$_2$H$_2$ system.[18] For this purpose, experiments at different collision energies are necessary.

Nevertheless, the explicit identification of the linear HBCC isomer is the first gas-phase assignment of this hydrogen-deficient species. Our proposed barrierless mechanism to **2** correlated nicely with matrix studies by Andrews et al., who found an increasing absorption signal of this isomer from a reaction of matrix trapped, cold B(^{2}P) atoms.[5] However, we concluded that the matrix isolated HBCCH isomer (**3**) was not the reaction product of translationally hot boron atoms inserting into the C—H bond but rather an isomerization product of **4**.

Finally, the large dipole moment of 3.97 debye as based on our electronic structure calculations makes HBCC an ideal search candidate for the first interstellar boron-bearing species. Interstellar boron atoms were detected with fractional abundances of 9.1×10^{-11} relative to hydrogen toward the Orion region and could react with acetylene to the HBCC isomer in this source.[19]

Acknowledgment

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