Untangling the Chemical Dynamics of the Reaction of Boron Atoms, $^{11}B(^{2}P_{j})$, with Diacetylene, $C_{4}H_{2}(X^{1}\Sigma_{g}{}^{+}) - A$ Crossed Molecular Beams and Ab Initio Study

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A crossed molecular beams experiment with ground state boron atoms, $B(^{2}P_{j})$, and diacetylene, $C_{4}H_{2}(X^{1}\Sigma_{g}^{+})$, was conducted at a collision energy of 21.1 ± 0.3 kJ mol⁻¹ under single collision conditions and combined with electronic structure calculations on the ${}^{11}BC_{4}H_{2}$ potential energy surface. Our combined experimental and computational studies indicate that the reaction proceeds without entrance barrier and involves indirect scattering dynamics. Three initial collision complexes, in which the boron atom adds to one or two carbon atoms, were characterized computationally. These intermediates rearranged via hydrogen shifts and/or successive ring-opening/ring closure processes on the doublet surface ultimately yielding a cyclic, C_{s} symmetric ${}^{11}BC_{4}H_{2}$ intermediate. The latter was found to decompose via atomic hydrogen loss to yield a cyclic ${}^{11}BC_{4}H(X^{1}A')$ isomer; to a minor amount, the cyclic intermediate isomerized via ring-opening to the linear HCCBCCH($X^{2}\Sigma_{g}^{+}$) molecule, which in turn emitted a hydrogen atom to yield the linear HCCBCC($X^{1}\Sigma^{+}$) molecule. The overall reactions to form these isomers were found to be exoergic by 55 and 61 J mol⁻¹, respectively, and involved rather loose exit transition states. On the basis of the energetics, upper limits of two energetically less stable species, the linear HBCCCC($X^{1}\Sigma^{+}$) and BCCCCH($X^{1}\Sigma^{+}$) species, were derived to be 12 and 2.2\%, respectively. The dynamics of this reaction are also compared with the reaction of ground state boron atoms with acetylene studied earlier in our group.

1. Introduction

The chemical dynamics of atomic boron reactions, $B(^{2}P_{i})$, with unsaturated hydrocarbons have received considerable attention due to the potential importance of this reaction class in combustion chemistry,1-5 material science,6-8 and astrochemistry.⁹⁻¹³ First, boron is considered a good candidate for jet engine fuel additives¹⁻⁵ given its high specific combustion energy, both in volumetric and gravimetric terms.^{5,14} Therefore, it is essential to understand the reaction of boron atoms with hydrocarbons as a part of the combustion process. Crossed molecular beam experiments provide the important prerequisite of single collision conditions and reactant state specificities to untangle reaction mechanisms under well-defined experimental conditions excluding wall effects.¹⁵ This technique has already been successfully applied in our laboratory for several boronhydrocarbon reactions as reviewed in ref 16 such as with the related acetylene molecule (C_2H_2) .¹⁷

Second, boron-carbon clusters and their partially hydrogenated counterparts have received considerable attention both theoretically and experimentally^{7,8,18,19} due to their importance in material science.^{6–8} The theoretical studies included structural calculations for the gas phase clusters containing one boron atom and four carbon atoms, that is, a molecule of the formula BC₄.^{20–23} In chemical vapor deposition (CVD) boron is used to produce boron-substituted carbon films,⁷ as boron doping improves the morphology and crystallinity of CVD diamondlike films.⁸ These films were used to produce photovoltaic Schottky ultraviolet detectors²⁴ and a window layer of amorphous silicon solar cells.²⁵ Boron-substituted carbon microporous films efficiently physisorb hydrogen and might find application in hydrogen storage.²⁶ Also, BC_x solid state phases drew attention due to their unique combination of excellent physical and chemical properties such as great hardness, high chemical inertness, and semiconducting properties.^{27,28} Graphite-phase and diamond-like phases of BC₃ are predicted to be superconductors.²⁹ Here, acetylene and diacetylene are among the major precursors in diamond-like films deposition.^{30,31} Therefore, data from the research conducted in our laboratory could be incorporated in the models of CVD processes of boron-doped diamond-like films.

Third, our research can contribute to better understand the interstellar boron chemistry. Atomic boron has been detected in the interstellar medium with fractional abundances of up to $2.5 \pm 0.9 \times 10^{-10}$ with respect to atomic hydrogen toward Orion and Ophiuchus (Serpens).9,10,32,33 Therefore, a study of atomic boron reactions can also help to untangle its reaction dynamics in more exotic, extreme environments where bimolecular collision conditions and temperatures as low as 10 K (cold molecular clouds) can reside. Closely related, since atomic boron, $B({}^{2}P_{i})$, is isoelectronic with singly ionized carbon atom, $C^{+}({}^{2}P_{i})$, an understanding of elementary boron atom reactions can also assist to understand the chemistry in weakly ionized hydrocarbon plasmas. Interaction of C^+ and carbon chains C_n is an important reaction in interstellar gas clouds models.^{11,12} Also, $C^+({}^2P_i)$ can contribute to the formation of polycyclic aromatic hydrocarbons participating in soot formation.¹³

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TABLE 1: Peak Velocities (v_p) and Speed Ratios (*S*) of the Intersecting Segments of the Crossed Supersonic Beams Together with Collision Energy (E_c) and Center-of-Mass Angle (Θ_{CM} , Relative to ¹¹B Beam Direction)

beam	$v_{\rm p} \ ({\rm m} \ {\rm s}^{-1})$	S	$E_{\rm c}~({\rm kJ}~{\rm mol}^{-1})$	$\Theta_{CM} \ (^{\circ})$
${}^{11}B({}^{2}P_{i})/He$	2070 ± 15	3.5 ± 0.1	21.1 ± 0.3	53.7 ± 1.0
$C_4H_2(X^1\Sigma_g^+)/Ar$	620 ± 15	26.0 ± 1.0		

To the best of our knowledge—based on a SciFinder literature research—there has been neither an experimental nor a theoretical study on the boron—diacetylene system to date. Here, we will report the very first results of the elementary boron reaction with diacetylene. Our study will give insight into unexplored BC_4H_2 and BC_4H potential energy surfaces (PESs) and help to unravel the contribution of these molecules in gas phase CVD processes where diacetylene is widely used as a precursor.^{17,34–37}

2. Experimental and Data Analysis

The elementary reaction of ground state boron atoms, ${}^{11}B({}^{2}P_{i})$, with diacetylene, $C_4H_2(X^1\Sigma_g^+)$, was studied in a universal crossed molecular beams machine under the single collision conditions.¹⁵ Briefly, the 30 Hz, 5–10 mJ, 266 nm output of a Spectra Physics GCR-270-30 Nd:YAG laser was focused onto a cylindrical surface of polycrystalline boron rod performing helical motion. A pulsed supersonic boron atom beam was generated in the primary source chamber by seeding the laser ablated boron atoms in a carrier gas beam released by a Proch-Trickl pulsed valve operating at 60 Hz and 80 μ s pulses with 4 atm backing pressure. After passing a skimmer, a four-slot chopper selected a segment of the seeded boron beam with a peak velocity of $v_p = 2070 \pm 15 \text{ m s}^{-1}$ and a speed ratio of S = 3.5 ± 0.1 . This part crossed a pulsed diacetylene beam produced in supersonic expansion of 5% C4H2 mixture in argon (99.9999%; Gaspro; 550 Torr total backing pressure) released by a second pulsed valve perpendicularly in the interaction region. The segment of the diacetylene beam was characterized by a peak velocity of $v_{\rm p} = 620 \pm 15 \text{ m s}^{-1}$ and a speed ratio of $S = 26 \pm 1$. A collision energy, $E_{\rm C}$, of 21.1 ± 0.3 kJ mol⁻¹ was obtained. The center-of-mass angle for ¹¹B/C₄H₂ system was $\Theta_{\rm CM} = 53.7 \pm 1.0^{\circ}$. Multiply ionized argon does not interfere with ¹¹B at m/z = 11. The characteristics of the reactant beams are summarized in Table 1. The reactively scattered species were monitored using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the molecules at 80 eV. This detector could be rotated within the plane defined by the primary and the secondary reactant beams to allow taking angular resolved TOF spectra at specific mass-to-charge (m/z) ratios. At each angle, up to 300 000 TOF spectra following each ablation laser shot were accumulated to achieve good signal-to-noise ratio. The recorded TOF spectra were then integrated and normalized to obtain a product angular distribution in the laboratory reference frame (LAB). To reveal the scattering dynamics, the laboratory data were transformed into the center-of-mass reference frame utilizing a forward-convolution routine.^{38,39} This iterative method initially assumes the angular flux distribution, $T(\theta)$, and the translational energy flux distribution, $P(E_{\rm T})$ in the center-ofmass system (CM). Laboratory TOF spectra and the laboratory angular distributions (LAB) were then calculated from the $T(\theta)$ and $P(E_{\rm T})$ functions, averaging over the apparatus functions and velocity distribution of the reactant beams. Best fits were obtained by iteratively refining the adjustable parameters in CM functions, $T(\theta)$ and $P(E_{\rm T})$. Reaction cross-section dependence on collision energy $\sigma(E_c) \propto E_c^{-(1/3)}$ has been adopted.⁴⁰ As for any scientific experiment, it is important to conduct a welldefined error analysis. The acceptable limits for the adjustable parameters in center-of-mass functions were defined as follows. Two χ^2 values, reflecting the deviation of the fit, were considered: the deviation from the experimentally derived LAB distribution, χ^2_1 , and the deviation from the TOF spectra at selected angles, χ^2_2 . Acceptable variation of any adjustable parameter from its optimal value should not raise either χ^2_1 or χ^2_2 by a defined fraction of corresponding optimal χ^2 value: $\chi^2_1 \leq (1 + \alpha_1)(\chi^2_1)_{\text{optimal}}$ and $\chi^2_2 \leq (1 + \alpha_2)(\chi^2_2)_{\text{optimal}}$. The best fit functions were utilized to produce a flux contour map, $I(\theta, u) = P(u) \times T(\theta)$, which plots the flux of the reactively scattered products (I) as a function of the center-of-mass scattering angle (θ) and product velocity (u). This image contains important information on the scattering process.

3. Electronic Structure Calculations

The pathways of the reaction of ground state boron atoms with diacetylene were investigated theoretically on the adiabatic ground state doublet surface. Multiple collision complexes were identified. Subsequently, probable low-energy isomerization and dissociation channels for each collision complex were searched for and characterized. The optimized geometries and harmonic frequencies of the intermediates, transition states, and dissociation products were obtained at the level of the hybrid density functional theory, the unrestricted B3LYP/cc-pVTZ.⁴¹⁻⁴⁴ Their CCSD(T)/cc-pVTZ energies with B3LYP/cc-pVTZ zero-point energy corrections were computed.^{45–48} The Gaussian 03 programs were employed in the electronic structure calculations.⁴⁹

4. Results

In the boron-diacetylene system, reactive scattering signal was recorded at mass-to-charge ratio, m/z, of 60, corresponding to the singly ionized ¹¹BC₄H species. Time-of-flight spectra (TOFs) at distinct scattering angles are shown in Figure 1. The red lines represent the best fits as described in the previous Experimental and Data Analysis section. Here, the experimental data are well fitted with a single-channel model. TOF taken at m/z = 59 overlapped after scaling of the intensities with those taken at m/z = 60 (Figure 2). Therefore, we can conclude that signal at m/z = 59 originates from dissociative ionization of the parent molecule at m/z = 60 and/or from the ionized ¹⁰BC₄H reaction product (the natural abundance of ¹⁰B is about 20%). We would like to note that the reaction with ¹⁰B is characterized by slightly different kinematics and hence a center-of-mass angle of 56.3°. In case of weakly exoergic reactions such as the one of ¹⁰B and ¹¹B with acetylene,¹⁷ this would results in distinct, nonoverlapping laboratory angular distributions. However, in case of the reaction of ground state boron with diacetylene, the relatively large exoergicity of the reaction "smears" out the distinct laboratory angular distributions in the same way as found in the reaction of boron atoms with methylacetylene studied earlier.34

An investigation of the energetics suggests that the molecular hydrogen channel is endoergic by 24 kJ mol⁻¹. Since the collision energy of our experiment (21 kJ mol⁻¹) is below the endoergicity of the reaction to form BC₄ ($X^2\Sigma_g^+$) + H₂($^1\Sigma_g^+$), it is sensible that we did not observe this channel experimentally. Therefore, the results indicate that only a product of the generic formula ¹¹BC₄H is formed in the bimolecular reaction of atomic boron with diacetylene by formally replacing a hydrogen atom by atomic boron. Figure 3 shows the laboratory angular distribution (LAB) of the ¹¹BC₄H (m/z = 60) product at a collision energy of 21.1 kJ mol⁻¹ derived by integrating the



Figure 1. Time-of-flight data at m/z = 60 for the indicated laboratory angles at a collision energy of 21.1 kJ mol⁻¹. The black line represents the experimental data, and the red line represents the fit.



Figure 2. Time-of-flight data at m/z = 60 (black line) and m/z = 59 (red line) recorded at the center-of-mass angle $\Theta_{CM} = 53.7^{\circ}$.

TOF spectra at the corresponding angles. The LAB distribution peaks at 51.5° , close to the center-of-mass angle of $53.7 \pm 1.0^{\circ}$, and spreads only over 20° range (fwhm). These patterns suggest that the reaction likely proceeds via indirect scattering dynamics involving a BC₄H₂ intermediate.

To obtain meaningful information on the dynamics of the reaction of ground state boron atoms with diacetylene, we are



Figure 3. Laboratory angular distribution of the ¹¹BC₄H product at m/z = 60. Squares and error bars indicate experimental data; the solid red line is calculated from the best fit distribution, and the two black curves correspond to the limits of acceptable fit. The center-of-mass angle is indicated by C.M.

transforming the data from the laboratory to the CM reference frame to yield the center of mass angular $(T(\theta))$ and translational



Figure 4. Center-of-mass translational energy flux distribution for the reaction ${}^{11}\text{B}({}^2\text{P}_j) + C_4\text{H}_2(X{}^1\Sigma_g^+)$ at a collision energy of 21.1 kJ mol⁻¹. The two black lines limit the range of acceptable fit; the red curve corresponds to the best fit.



Figure 5. Center-of-mass angular flux distribution for the reaction ${}^{11}\text{B}(^2\text{P}_j) + C_4\text{H}_2(X^1\Sigma_g^+)$ at a collision energy of 21.1 kJ mol^{-1}. The two black lines limit the range of acceptable fit; the red curve corresponds to the best fit.

 $(P(E_T))$ energy flux distributions (Figures 4 and 5). Best fits of the LAB distributions and the TOF data could be achieved with $P(E_{\rm T})$ values extending to a maximum translational energy release (E_{max}) of 70⁻¹³₊₄ kJ mol⁻¹. Extending the tail by 10 kJ mol⁻¹ at a flux level of about 0.05 or lower has no influence on the fit. E_{max} is the sum of the reaction exoergicity plus the collision energy. Therefore, by subtracting the collision energy from the high energy cutoff, we are left with experimental exoergicity of 49^{-13}_{+14} kJ mol⁻¹. This experimental value can be utilized at a later stage to be compared with ab initio calculations, thus identifying the structural isomer(s) formed. Second, the $P(E_{\rm T})$ s were found to peak away from zero translational energy at about 15 kJ mol⁻¹. This pattern might indicate the existence of a rather loose exit transition state when the BC₄H₂ reaction intermediate decomposes via atomic hydrogen elimination to form the BC4H product. Recall that a barrier-less reaction is expected to result in a center-of-mass translational energy distribution peaking at zero translational energy. Finally, we can calculate the average fraction of the available energy

channeling into the translational degrees of the products to be about 31%; this order of magnitude is indicative of indirect scattering dynamics.

Additional information on the chemical dynamics can be obtained from the center-of-mass angular distribution. Here, the $T(\theta)$ is moderately forward scattered with respect to the ¹¹B beam and extends over the complete angular range. The latter suggests the involvement of a ¹¹BC₄H₂ intermediate and hence indirect scattering dynamics. Further, the forward scattering indicates that, in the fragmenting complex, the incorporated boron atom and the leaving hydrogen atom must be located on the opposite sides of the rotational axis; the forward scattering is also reflected in the flux contour plot as depicted in Figure 6. —ased on the intensity ratio at the poles at 180° and 0°, we can estimate the lifetime, τ , of the BC₄H₂ complex within the osculating complex model⁵⁰ through eq 1 with ($I(0^{\circ})$)/($I(180^{\circ})$) = $1.5\pm0.3^{\circ}$ as extracted from Figure 5.

$$\frac{I(180^0)}{I(0^0)} = \exp\left(-\frac{t_{\rm rot}}{2\tau}\right) \tag{1}$$

This suggests a lifetime, τ , of about $1.2^{\pm0.6}_{-0.6} t_{\text{rot}}$, with t_{rot} being the rotational period of the reaction intermediate of $t_{\text{rot}} = 2\pi I_i/L_{\text{max}}$, where I_i represents the moment of inertia of the complex rotating around the *i*th principal axis (*i* = a, b, c), and L_{max} the maximum orbital angular momentum. Further, the CM angular distribution depicts a slight dip at 90°; this could indicate geometrical constrains of the decomposing complex, that is, an emission of the hydrogen atom within the plane of the decomposing, rotating complex.⁵⁰

5. Discussion

To elucidate the chemical dynamics of multiatom reactions, it is often useful to combine electronic structure calculations with the experimental data. Recall that, for instance, ab initio calculations provide possible reaction pathways. However, this does not expose any information on the actual reaction pathways, if, for instance, dynamical factors are involved, if the system is kinetically controlled, or if the system does not follow an expected RRKM behavior. Therefore, ab initio calculations can never replace experiments, but should be rather used in combination with experimental crossed beam data to elucidate the underlying dynamics. Here, our ab initio calculations located 16 possible ${}^{11}BC_4H$ product isomers (p1-p16). Table S1 (Supporting Information) compiles the structures, electronic states, and energetics with respect to the separated reactants. The formation of the isomers **p1** and **p2** is exoergic and slightly endoergic for p3 and p4 at the CCSD(T)/cc-pVTZ level of theory with UB3LYP/cc-pVTZ zero-point energy corrections. The isomers p5-p16 are significantly higher in energy and—with the exception of p8, p10 and p7-comprise of complex, often polycyclic structures with significant ring tension. Considering our collision energy of 21 kJ mol⁻¹, only products **p1-p4** might be formed; therefore, the discussion and the potential energy surface (Figure 7) only address these structures. Here, a comparison of the computed exoergicitiesaccounting for an accuracy of $\pm 8 \text{ kJ mol}^{-1}$ for the level of theory reported—with the experimentally obtained one of $49^{-13}_{\pm 14}$ kJ mol⁻¹, suggests that isomer **p1** (-61 ± 8 kJ mol⁻¹) and/or $p2 (-55 \pm 8 \text{ kJ mol}^{-1})$ are the likely reaction products. Within the error limits, products p3 and p4 can be excluded as major contributors, but might present minor channels. Upper limits of about 12 and 2.2% can be derived as integrals of $P(E_T)$ from



Figure 6. Best fit of the (top) two- and (bottom) three-dimensional flux contour maps for the reaction ${}^{11}B({}^{2}P_{j}) + C_{4}H_{2}(X{}^{1}\Sigma_{g}{}^{+})$ at a collision energy of 21.1 kJ mol⁻¹. Units are m s⁻¹.

zero to the maximum translational energies based on enthalpies of formation from Table S1 and collision energy from Table 1. The following discussion will focus initially on the isomers **p1** and **p2**.

Our electronic structure calculations suggest three barrierless addition pathways of the electrophilic boron atom to the π -electron density of the diacetylene molecule (Figure 7). Here, $B(^{2}P_{i})$ either adds to two carbon atoms, simultaneously leading to intermediate [1] (addition to C1 and C2), or only to one carbon atom (C1 or C2), forming intermediates [2] and [3], respectively (Figure 7; Table S2). On the basis of the structures alone, one might assume that atomic boron can also add to C2 and C3 of diacetylene forming a $C_{2\nu}$ symmetric intermediate [4] with a ${}^{2}B_{2}$ electronic state. Within this symmetry and electronic state, a careful scan of the surface (pulling away the boron atom from diacetylene) showed that the energy is sharply rising; this indicates that the ²B₂ electronic state correlates with an excited state of the boron plus diacetylene reactants. Among these structures, [1] is the most stable one. These initial collision complexes can isomerize. Intermediates [2] and [3] can undergo ring closure via barriers of only 3 and 7 kJ mol⁻¹, yielding [1]. Isomer [4] can undergo ring-opening via a barrier or 8 kJ mol⁻¹ to [3]. In addition to the rearrangements among [1]-[3], these initial collision complexes can undergo further isomerization. Structure [1] can either form a bicyclic isomer [6] or a hydrogenbridged structure [7], which in turn rearranges to [9]. Intermediate [6] can undergo ring-opening to form [8]. Considering the barriers involved, the sequence $[1] \rightarrow [6] \rightarrow [8]$ should be preferred compared to $[1] \rightarrow [7] \rightarrow [9]$. The rearrangements of intermediate [2] are very interesting. Here, three pathways have been identified proceeding via the sequences $[2] \rightarrow [6] \rightarrow [8]$, $[2] \rightarrow [5] \rightarrow [6] \rightarrow [8]$, and $[2] \rightarrow [11]$. Considering the barriers, it is likely that [2] isomerizes preferentially to [1] and ultimately to [8] via [6]. The location of the barriers of 7 kJ mol⁻¹ versus 35 kJ mol⁻¹ suggests that isomer [3] rearranges preferentially to [1] compared to [6]. Even though [6] might present a minor pathway, its ultimate fate is dictated by a ring-opening to [8]. The intermediate [4] can rearrange to [3] or via ring-opening to the linear structure [10]. We can see that collision complexes [1]-[3] are expected to yield preferentially isomer [8] and—from [1]-to a minor extent [9]. On the other hand, [4] can also undergo ring-opening to [10]. What is the fate of these intermediates [8], [9], and [10]? A closer look at the computed potential energy surface suggests that [8] either isomerizes to [10] followed by hydrogen atom loss to form p1 or emits a hydrogen atom to yield **p2** via a barrier located 7 kJ mol⁻¹ above the separated reactants. Intermediate [9], which was suggested to be formed to a lesser extent, can only rearrange to the linear molecule [11], which in turn releases a hydrogen atom from the boron or carbon atom to form **p4** or **p3**, respectively. Here, it is important to note that, based on the computed energetics of the reaction and the experimentally derived reaction energies, p3 and p4 were suggested to be only minor products. This correlates well with our computations indicating that p3 and p4 can only be formed via unimolecular decomposition of chemically activated [11], which in turn arose from rearrangement of [9]; the latter was identified—based on the inherent barriers to isomerization-as a minor reaction pathway in the isomerization of [1]. Therefore, both the experimental findings and computations are consistent suggest that p3 and p4-formed from [11] via [9]—are only minor reaction products, whereas



Figure 7. Computed ${}^{11}BC_4H_2$ potential energy surface (PES) of the reaction of ground state boron atoms with diacetylene leading to the four lowest energy ${}^{11}BC_4H$ isomers **p1**–**p4**. The structures, point groups, bond lengths, and angles of the products and intermediates are compiled in Tables 2 and 3 of the Supporting Information.



Figure 8. Computed structures of the transition states, projected onto the rotational plane, connecting intermediate [10] with p1 plus atomic hydrogen and [8] with p2 plus a hydrogen atom. The viewing direction is parallel to the total angular momentum vector. Bond lengths and angles are given in nanometers and degrees, respectively. The hydrogen atoms are shown to leave the decomposing complex within the rotational plane, that is, the paper plane.

p1 (from **[8]** via **[10]**) and/or **p2** (from **[8]**) should present the dominant products.

How can we discriminate if **p1** and/or **p2** are formed (Figure 7)? Recall that product **p1** can be only formed via an atomic hydrogen loss from [10]. This isomer is linear and can only be excited to B-like rotations. Since this structure belongs to the $D_{\infty h}$ point group, intermediate [10] must be classified as a symmetric intermediate. The latter can lose a hydrogen atom with equal probability from either carbon atom to be ejected into θ^0 and $\pi - \theta^0$. In the CM system, this equal probability results always in a forward-backward symmetric CM angular distribution⁵⁰ as already observed in the unimolecular decomposition of, for instance, linear, singlet diacetylene⁵¹ and the C_2 symmetric triplet propargylene intermediate.⁵² Therefore, a formation of *only* the thermodynamically most stable isomer **p1** *cannot* explain the experimentally observed forward-peaking

CM angular distribution. Consequently, **p2** must be formed in the reaction of ground state boron atoms with diacetylene. Here, isomer [8] belongs to the C_s point group and hence is clearly nonsymmetric. Therefore, the involvement of the decomposing complex [8] and hence formation of p2 plus atomic hydrogen can account for the asymmetric CM angular distribution as observed experimentally. Nevertheless, a forward-backward symmetric, second channel arising from the fragmentation of [10] to p1 plus a hydrogen atom cannot be excluded since a superposition of a forward-backward and a forward scattered distribution always result in a forward scattered CM angular distribution. Recall that the CM angular distribution depicts a small dip at 90°. This could reflect geometrical constraints and hint to an ejection of the hydrogen atom preferentially within the plane of the fragmenting intermediate(s). Here, a closer look at the transition states connecting [8] with p2 and [10] with p1



Figure 9. Location of the three principal rotational axes of intermediate [8].

(Figure 8) indicate that in both cases the hydrogen atom leaves within the rotational plane. Also, the rather loose nature of the exit transition states is reflected in the only moderate off-zero peaking of the CM translational energy distribution. On the basis of these considerations, we would like to propose that **p2** presents the dominant product of the title reaction formed via indirect scattering dynamics through the decomposing intermediate **[8]**. The latter could also isomerize to **[10]**, which in turn fragmented to a lesser amount to form p1 plus atomic hydrogen. On the basis of the rotational axes of intermediate **[8]** and the forward-peaking of the center-of-mass angular distribution, it is likely that **[8]** is excited to C-like rotations (Figure 9). This fulfils the requirement that for the forward-peaked angular distribution, the incorporated boron atom and leaving hydrogen are located on opposite sides of the rotational axis.

The dynamics of this reaction are to some extent similar to those observed in the reaction of ground state boron atoms with acetylene studied earlier in our laboratory.¹⁷ Here, two channels were observed to be open: the formation of the linear HB- $CC(X^{1}\Sigma^{+})$ isomer and a cyclic ¹¹BC₂H(X¹A') structure. This cyclic structure links very nicely to the cyclic isomer **p2** as observed in the present study by formally replacing the hydrogen atom in c-¹¹BC₂H(X¹A') by an ethynyl (CCH) group. Likewise, the decomposing c-¹¹BC₂H₂ complex forming c-¹¹BC₂H(X¹A') in the reaction of boron with acetylene can be nicely correlated with intermediate **[8]** in the present reaction by replacing the hydrogen atom at the boron atom by the ethynyl (CCH) group.

For completeness, it should be noted that the reaction intermediates could also fragment via carbon–carbon bond rupture processes, leading preferentially to the ethynyl group loss (CCH). This involves the channels $CCH(X^2\Sigma^+) + HBCC(X^2\Sigma^+)$ and $CCH(X^2\Sigma^+) + c-BC_2H(X^2A')$. The reactions are endoergic by 13 and 9 kJ mol⁻¹, respectively. Considering our collision energy of 21 kJ mol⁻¹, and the reaction energies of the competing hydrogen loss channels together with the exit barriers, the carbon–carbon bond rupture processes are expected to be of minor importance.

6. Conclusions

We have conducted the crossed molecular beams experiment of ground state boron atoms with diacetylene at a collision energy of 21.1 ± 0.3 kJ mol⁻¹ under single collision conditions and combined our experimental results with electronic structure calculations on the ¹¹BC₄H₂ potential energy surface. The reaction proceeds without entrance barrier via indirect scattering dynamics under the involvement of multiple ¹¹BC₄H₂ reaction intermediates. Three initial collision complexes ([1]–[3]) were identified computationally. These collision complexes were found to isomerize via multiple rearrangements yielding predominantly a cyclic, C_s symmetric intermediate [8] on the doublet surface; energetically spoken, this structure presents the global minimum on the¹¹BC₄H₂ potential energy surface. This intermediate fragmented mainly via atomic hydrogen loss to form the cyclic ${}^{11}BC_4H(X^1A')$ isomer **p2**; without a decomposition of the CM angular distribution into two components, it is not possible to quantify the contribution of the HCCBCC($X^{1}\Sigma^{+}$) molecule. The exit transition states involved were found to be rather loose; this was also reflected into a moderate off-zero peaking of the CM translational energy distribution. Therefore, based on the reactions of boron atoms with acetylene and diacetylene, which lead at least to the formation of a cyclic isomer of the generic form c-BC₂X, in which X is connected to the boron atom and presents either an H atom or the CCH unit, we might predict that upon reaction with more complex polyynes, the $-(C \equiv C)_n H$ unit might act as a spectator ultimately leading to at least cyclic $c-BC_2-(C\equiv C)_nH$ isomers.

Acknowledgment. This project was supported by Air Force Office of Scientific Research (A9550-09-1-0177). We thank Professor Alexander Mebel (Florida International University) for valuable discussions. Computer resources at the National Center for High-performance Computer of Taiwan were utilized in the calculations.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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JP1065067