Directed Gas-Phase Formation of the Ethynylsulfidoboron Molecule

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S *Supporting Information*

ABSTRACT: As a member of the organo sulfidoboron (RBS) family, the hitherto elusive ethynylsulfidoboron molecule (HCCBS) has been formed via the bimolecular reaction of the boron monosulfide radical (BS) with acetylene (C_2H_2) under single collision conditions in the gas phase, exploiting the crossed molecular beams technique. The reaction mechanism follows indirect dynamics via a barrierless addition of the boron monosulfide radical with its boron atom to the carbon atom of the acetylene molecule, leading to the *trans*-HCCHBS intermediate. As predicted by ab initio electronic structure calculations, the initial collision complex either isomerizes to its *cis*-form or undergoes a hydrogen atom migration to form H_2CCBS. The *cis*-HCCHBS intermediate either isomerizes via hydrogen atom shift from the carbon to the boron atom, leading to the HCCBHS isomer, or decomposes to ethynylsulfidoboron (HCCBS). Both H_2CCBS and HCCBHS intermediates were predicted to fragment to ethynylsulfidoboron via atomic hydrogen losses. Statistical (RRKM) calculations report yields to form the ethynylsulfidoboron molecule from *cis*-HCCHBS, H_2CCBS, and HCCBHS to be 21%, 7%, and 72%, respectively, under current experimental conditions. Our findings open up an unconventional path to access the previously obscure class of organo sulfidoboron molecules, which are difficult to access through "classical" formation.
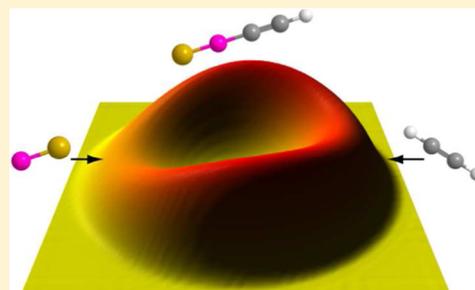
1. INTRODUCTION

During the last decades, molecules carrying multiple bonds to third row atoms such as to main group XIV, XV, and XVI elements including silicon (Si), phosphorus (P), and sulfur (S) have been widely explored, leading to novel concepts in chemical bonding and the formation of exotic molecules carrying carbon−silicon, carbon−phosphorus, silicon−nitrogen, phosphorus−nitrogen, and sulfur−nitrogen bonds (Scheme 1).

Scheme 1. Typical Bond Distances for Carbon−Silicon, Carbon−Phosphorus, Silicon−Nitrogen, Phosphorus−Nitrogen, and Sulfur−Nitrogen Bonds

However, organo sulfidoboron species (RBS), molecules carrying the boron monosulfide moiety (BS) and an organic substituent (R), have remained essentially uncharacterized because of difficulty in preparation, sensitivity to air, short lifetimes, and tendency to form trimers.[1,2]

The stem compound thioborine (HBS) was first characterized in 1967 via a high temperature gas-phase reaction between crystalline boron and hydrogen sulfide (H_2S) at 1400 K.[1,3] The rotational spectra proposed boron−hydrogen and boron−sulfur bond distances of 116.96 and 159.78 pm, respectively (Scheme 2).[4,5] Consecutive electronic structure

Scheme 2. Bond Distances of Boron−Hydrogen and Boron−Sulfur Bonds in Thioborine (HBS)
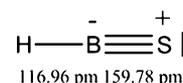
calculations proposed a polar triple bond character for the boron−sulfur bond,[6] which results from a dative π-bond by donation of one of the lone electron pairs from the sulfur atom to boron atom.[7] The energy difference between HBS and its thermodynamically less stable HSB isomer was determined to be 258 kJ mol^{-1}.[8,9] These studies have been extended to form halogenated sulfidoboron molecules (XBS; X = F, Cl, Br) by passing the corresponding disulfurdihalides (S_2X_2) or sulfur tetrafluoride (SF_4) over solid boron.[10−16]

Methylsulfidoboron (CH_3BS), the only organo sulfidoboron molecule characterized to date, was accessed by Kroto in 1978

as a short-lived product of the high temperature gas-phase reaction between dimethyl disulfide (CH_3SSCH_3) and crystalline boron.[2] The observed bond distance of 160.22 pm is in close agreement with that of 159.78 pm as observed in thioborine (HBS) and reflects the tendency to slightly increase the bond distance upon substituting a hydrogen atom by a methyl group.[17] However, the short lifetime of methylsulfido-boron and the tendency to trimerize limited the versatility of this approach to systematically form organo sulfidoboron molecules. Therefore, as of today, organo sulfidoboron species represent one of the least explored classes of organic molecules, whose directed formation has remained elusive.

Here we present a novel and versatile approach to form monomers of organo sulfidoboron molecules in the gas phase under single collision conditions exploiting the crossed molecular beams approach.[18−20] By crossing supersonic beams of the boron monosulfide radical (BS) in its $^2\Sigma^+$ electronic ground state with acetylene (C_2H_2; $X^1\Sigma_g^+$), we are presenting a proof-of-concept study that ethynylsulfidoboron (HCCBS) can be formed in the gas phase via a free radical substitution reaction (S_R) by replacing atomic hydrogen with the boron monosulfide moiety (reaction 1). This technique represents a powerful experimental method to conduct chemical reactions in the gas phase and to observe the outcome from the reaction of a single boron monosulfide radical with only one acetylene molecule in forming highly reactive molecules, which are difficult to form by classical organic chemistry. Because this reaction is conducted under single collision conditions, i.e., conditions without the possibility of successive reaction of the ethynylsulfidoboron molecule, a successive trimerization is eliminated (reaction 2), and only the monomer is formed under controlled conditions. The experimental studies are merged with electronic structure calculations to gain also insights into the chemical bonding of the newly formed ethynylsulfidoboron molecule (HCCBS), in particular with respect to the concept of isovalency with the extensively characterized ethynylboron monoxide molecule (HCCBO).

$$HCCH + BS \rightarrow HCCBS + H \qquad (1)$$

$$3HCCBS \rightarrow (HCCBS)_3 \qquad (2)$$

2. EXPERIMENTAL SECTION

The gas-phase reaction between the boron monosulfide radical (BS; $X^2\Sigma^+$) and acetylene (C_2H_2; $X^1\Sigma_g^+$) was carried out at the molecular level under single collision conditions exploiting a crossed molecular beams machine.[18−20] A pulsed supersonic beam of boron monosulfide radicals was generated in situ by laser ablation of a boron rod at 266 nm[21] and subsequently entraining the ablated boron atoms into carbon disulfide (99.9%; Fisher Scientific) seeded in 2.7 atm backing pressure of helium gas (99.9999%; Airgas Gaspro). The boron monosulfide radical beam was collimated by a skimmer and velocity-selected by a chopper wheel (peak velocity $v_p = 1233 \pm 20$ m s^{-1}; speed ratio $S = 3.0 \pm 0.3$) and perpendicularly intersected a supersonic beam of pure acetylene gas (C_2H_2; Air Liquide; 99.9% purity after removal of acetone via zeolite traps and an ethanol−dry ice bath) with a peak velocity of 883 ± 15 m s^{-1} and speed ratio of 7.0 ± 0.3 in the scattering chamber, at a total collision energy of 19 ± 1 kJ mol^{-1}. The reaction products were monitored by a rotatable quadrupole mass spectrometer after electron impact ionization of the neutral products at 80 eV in an ultrahigh vacuum chamber system held at a pressure of a few 10^{-12} Torr. The velocity distributions of the products were collected through the angular-resolved time-of-flight (TOF) technique,

that is, recording the arrival time of the ionized products at well-defined mass-to-charge ratios (m/z), at different scattering angles.

3. RESULTS AND DISCUSSION

TOF spectra and reactive scattering signals were collected, accounting for the natural abundances of boron ($^{11}B/^{10}B$) and sulfur (^{34}S, ^{33}S, ^{32}S) in the boron monosulfide reactant with masses ranging from 45 amu ($^{11}B^{34}S$) to 42 amu ($^{10}B^{32}S$). The TOF spectra of potential atomic and molecular hydrogen loss channels upon reaction of boron monosulfide with acetylene (C_2H_2; 26 amu) were probed from m/z of 70 ($^{11}B^{34}SC_2H^+$) to m/z of 66 ($^{10}B^{32}SC_2^+$) and were found to be superimposable after scaling. A complete angular distribution was obtained for ions at m/z of 68 ($^{11}B^{32}SC_2H^+$), where the signal-to-noise ratio was the best (Figure 1). Because the laboratory data could be fit
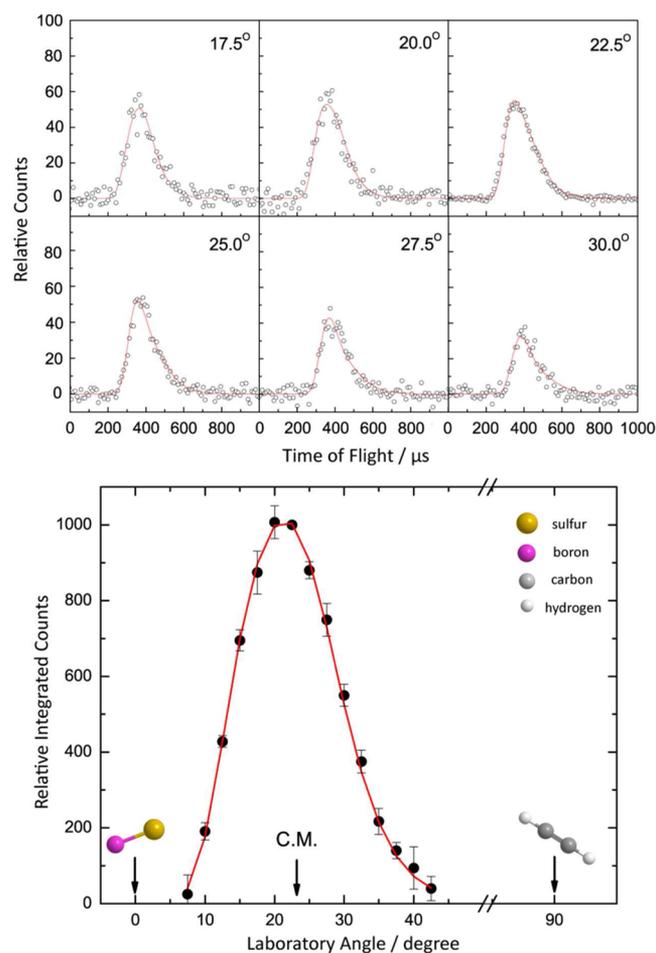
Figure 1. Selected time-of-flight (TOF) spectra at mass-to-charge (m/z) ratio of 68 ($^{11}B^{32}SC_2H^+$) (top), and the corresponding laboratory angular distribution (bottom) for the reaction of boron monosulfide with acetylene. The circles represent the experimental data points, while the solid lines represent the best fits.

with a mass combination of the products of 68 amu ($^{11}B^{32}SC_2H$) and 1 amu (H), we can conclude that at least an atomic hydrogen channel is open and that a product of the molecular formula $^{11}B^{32}SC_2H$ (hereafter: BSC_2H) is formed. The corresponding laboratory angular distribution peaks close to the center-of-mass (C.M.) angle of $23.4° \pm 0.9°$ and spans a scattering range from $7.5°$ to $42.5°$. These findings suggest an indirect reaction mechanism via the formation of BSC_2H_2

collision complex(es).[22] However, our objective is not only to assign the molecular formula of the reaction product, but also to rationalize the chemical structure of the isomer(s) and the reaction mechanism involved in the formation of the novel molecule(s). To complete these goals, it is vital to extract information on the chemical dynamics from the experimental data. This is accomplished by exploiting a forward convolution routine[23−25] to convert the laboratory data (TOF spectra, laboratory angular distribution) of the BSC_2H product(s) at m/z of 68 into the center-of-mass reference system. This approach produces two "best-fit" functions: the center-of-mass translational energy flux distribution $P(E_T)$ and the angular flux distribution $T(\theta)$ (Figure 2).
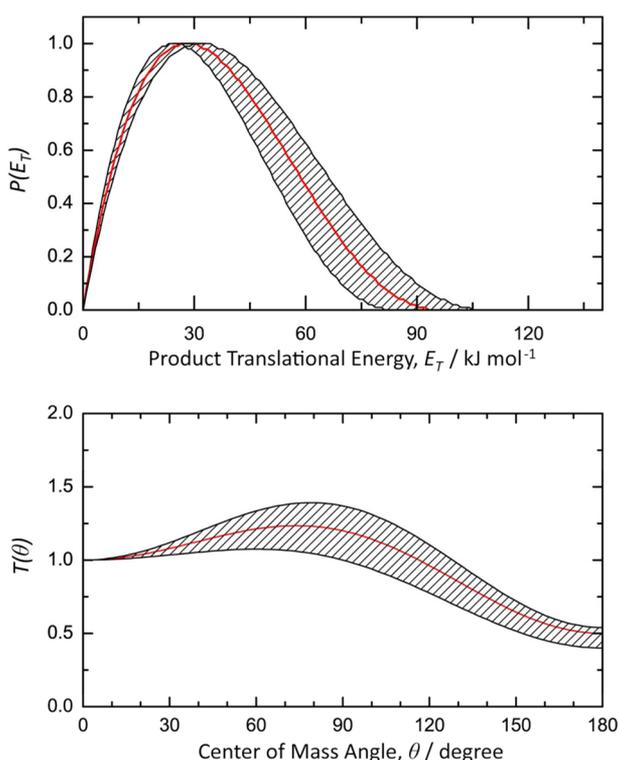
Figure 2. Center-of-mass translational energy flux distribution ($P(E_T)$, top) and angular flux distribution ($T(\theta)$, bottom) for the formation of the $^{11}B^{32}SC_2H$ product(s) in the reaction of boron monosulfide with acetylene. The hatched areas account for the experimental error limits.

Considering the center-of-mass translational energy flux distribution, $P(E_T)$, the maximum translational energy ($E_{max} = 90 \pm 15$ kJ mol^{-1}) of the products helps to identify the nature of the BSC_2H isomer(s). Note that for molecules born without rovibrational excitation, E_{max} presents the sum of the collision energy and the reaction exoergicity. Therefore, if we subtract the collision energy from E_{max}, the reaction to form BSC_2H plus atomic hydrogen is found to be exoergic by 71 ± 16 kJ mol^{-1}. The formed BSC_2H product(s) can be revealed by a comparison of the experimentally determined reaction exoergicity (71 ± 16 kJ mol^{-1}) with the energetics obtained from electronic structure calculations for distinct BSC_2H isomers (Figure 3). Here the geometries of various species involved in the reaction were explored via ab initio electronic structure calculations. The intermediates, transition states, and dissociation products are characterized such that their optimized geometries and harmonic frequencies are obtained

at the level of the hybrid density functional theory (Table S1, Supporting Information), the unrestricted B3LYP/cc-pVTZ,[26,27] and the energies are refined with the coupled cluster[28−31] CCSD(T)/cc-pVTZ method with B3LYP/cc-pVTZ zero-point energy corrections (Table S2, Supporting Information). The barrierless formation of the collision complex is confirmed by intrinsic reaction coordinate calculations (IRC) at unrestricted B3LYP/cc-pVTZ level of theory along the C−B bond distance. The GAUSSIAN 03 program is utilized in the electronic structure calculations; relative energies are expected to be accurate within ±5 kJ mol^{-1}.[32]

At the CCSD(T)/cc-pVTZ level of theory, the theoretical investigations indicate the existence of four singlet BSC_2H isomers (**p1** to **p4**): the linear ethynylsulfidoboron (HCCBS; **p1**), the isoethylnylsulfidoboron (CCHBS; **p2**), the four-membered ring structure (c-BSC_2H; **p3**), and the bent ethynylisosulfidoboron (HCCSB; **p4**). The computations predict that ethynylsulfidoboron (HCCBS) (**p1**) is more stable by 361 kJ mol^{-1} compared to the ethynylisosulfidoboron (HCCSB) isomer (**p4**). The preferential stability of the ethylnylsulfidoboron structure compared to that of ethynyliso-sulfidoboron matches well with the previous study by Mebel et al.[8] proposing that HBS is thermodynamically preferred by 258 kJmol^{-1} compared to the HSB isomer. Further, our computations indicate that the overall reaction to form ethynylsulfidoboron plus atomic hydrogen is exoergic by 72 ± 5 kJ mol^{-1}; this data agrees very well with the experimentally determined reaction exoergicity of 71 ± 16 kJ mol^{-1}. The other products, **p2**, **p3**, and **p4** are energetically not accessible under single collision conditions; the computed reaction endoergic-ities of 127, 178, and 289 kJ mol^{-1} could not be compensated by the collision energy of only 19 kJ mol^{-1}. Therefore, we can deduce that ethynylsulfidoboron (HCCBS) presents the only reaction product formed at $m/z = 68$, and we can conclude that our experiments formed and observed the linear ethynylsulfi-doboron molecule (HCCBS) via a bimolecular reaction under single collision conditions.

We would like to now untangle the reaction mechanism forming ethynylsulfidoboron. This also requires an inspection of the center-of-mass angular flux distribution $T(\theta)$. This function depicts flux over the complete scattering range from 0° to 180° as indicative of an indirect reaction mechanism and the formation of a reaction intermediate (complex) of the chemical formula C_2H_2BS.[22] Further, the "best-fit" depicts an asymmetric profile with an enhanced flux in the forward-scattering direction with respect to the boron monosulfide radical beam peaking at about 85° with an intensity ratio at the poles, $I(180°)/I(0°)$, of 0.4 to 0.6. This finding suggests that the lifetime of the C_2H_2BS intermediate is comparable to its rotational period.[33] Finally, the peak intensity at around $\theta = 85°$ indicates geometrical constraints upon the decomposition of the C_2H_2BS complex with a preferred direction of the atomic hydrogen emission that is close to parallel to the total angular momentum vector and perpendicular to the rotational plane of the decomposing complex.[33] The center-of-mass translational energy flux distribution $P(E_T)$ provides additional but crucial information on the reaction mechanism leading to ethynylsulfidoboron. Here the center-of-mass translational energy flux distribution depicts a distribution maximum of 20 to 40 kJ mol^{-1}, indicating the presence of at least one tight transition state, when the hydrogen atom is leaving the decomposing C_2H_2BS inter-mediate to form ethynylsulfidoboron.[22] Recalling the concept
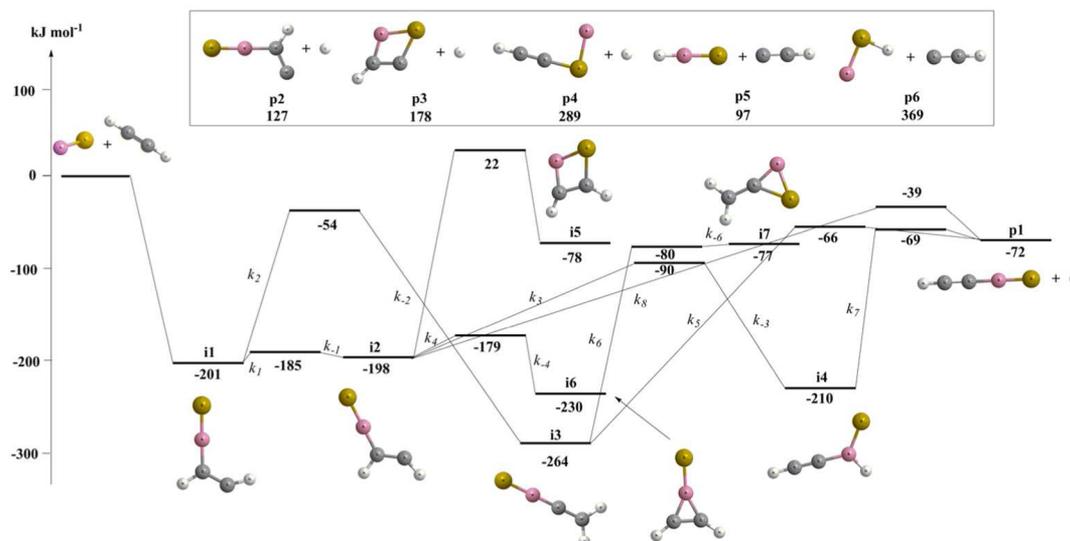
Figure 3. Schematic representation of the computed $C_2H_2{}^{11}B{}^{32}S$ potential energy surface (PES).

of microscopic reversibility,[22] an entrance barrier of this order of magnitude is expected in the case of reverse reaction via an addition of a hydrogen atom to ethynylsulfidoboron. Considering that the hydrogen atom adds to a closed shell molecule, the entrance barriers for an addition of atomic hydrogen to a carbon−carbon triple bond and double bond in acetylene and ethylene have been determined to be 15 and 19 kJ mol^{-1}, respectively.[34]

Now we are combining these findings with electronic structure calculations and recommend the structures of the reaction intermediates and the inherent reaction mechanism to form ethynylsulfidoboron (HCCBS) in the gas phase as a result of a bimolecular collision. Our computations indicate that the boron monosulfide radical adds without entrance barrier to the carbon−carbon triple bond of the acetylene molecule, leading to intermediate **i1** *trans*-HCCHBS. Intermediate **i1** either isomerizes via a small barrier of only 16 kJ mol^{-1} to its *cis*-form **i2** or undergoes a hydrogen atom shift from the C1 to the C2 carbon atom of the acetylene moiety to yield **i3** (H$_2$CCBS) over a barrier of 147 kJ mol^{-1}. Intermediate **i2** then can either isomerize to **i4**, **i5**, and **i6** over barriers of 108 kJ mol^{-1}, 220 kJ mol^{-1}, and 19 kJ mol^{-1}, respectively, or undergo an atomic hydrogen emission via an exit barrier of 33 kJ mol^{-1} with respect to the product system of ethynylsulfidoboron and hydrogen (H). Noteworthy, the transition state for the atomic hydrogen loss from **i2** could not be located at the B3LYP/cc-pVTZ level but was found using the coupled clusters CCSD/cc-pVTZ method. Both **i3** and **i4** can undergo unimolecular decomposition to yield ethynylsulfidoboron via atomic hydrogen losses by passing loose exit transition states located only 6 and 3 kJ mol^{-1} above the separated product system. Note that the computed geometries of the exit transition states suggest that the hydrogen atom is emitted at an angle of about 88°, 83°, and 91° upon the decomposition of **i2**, **i3**, and **i4**, respectively. Considering the center-of-mass angular flux distribution, these geometrical features match very well with our experimentally predicted sideways scattering at a peaking angle of about 85° with respect to the rotational plane of the decomposing intermediate. Assuming that the available energy is equilibrated among molecular degrees of freedom before the reaction occurs and considering that energy is conserved such as in molecular

beam experiments, the rate constants for the reaction steps can be predicted by RRKM theory as described previously (Table S3, Supporting Information).[35,36] These calculations suggest that, the product ethynylsulfidoboron can be formed via unimolecular decompositions of **i2**, **i3**, and **i4** at branching ratios of about 21%, 7%, and 72%, respectively (Table S4, Supporting Information). Note that intermediates **i2** and **i3** can also isomerize to exotic cyclic reaction intermediates **i5** to **i7**. However, these species cannot decompose via endoergic atomic hydrogen loss pathways but rather react back to **i2** and/or **i3** and result in "recycling" of these intermediates. To summarize, the boron monosulfide radical reacts with acetylene via an indirect reaction mechanism through a barrierless addition with its boron atom to the π electron density at one carbon atom of acetylene, forming a C$_2$H$_2$BS intermediate **i1**, which isomerizes to either **i2** or **i3**. Intermediate **i2** either isomerizes to **i4** prior to further decomposition via atomic hydrogen loss involving exit barriers of 3 kJ mol^{-1} with the formation of ethynylsulfidoboron (72%) or undergoes hydrogen loss to form ethynylsulfidoboron via a barrier of 33 kJ mol^{-1} (21%). Hydrogen elimination of **i3** involves an exit barrier of 6 kJ mol^{-1} but contributes little to the formation of ethynylsulfidoboron (7%).

It is attractive to contrast the reaction mechanism of the boron monosulfide radical (BS; $X^2\Sigma^+$) plus acetylene (C$_2$H$_2$; $X^1\Sigma_g^+$) with the isoelectronic reaction between the boron monoxide radical (BO; $X^2\Sigma^+$) with acetylene (C$_2$H$_2$; $X^1\Sigma_g^+$) studied earlier in our group.[19] This reaction was also suggested to follow indirect dynamics via a barrierless addition of the boron monoxide radical with its boron atom to one carbon atom of the acetylene molecule, forming the *cis/trans* HCCHBO intermediate(s). The *cis*-structure can emit a hydrogen atom through a tight exit transition state, forming the ethynyl boron monoxide molecule. The initial reaction intermediate can also undergo an atomic hydrogen migration to yield H$_2$CCBO prior to the decomposition of the latter via a tight exit transition state, forming ethynyl boronmonoxide. Comparing the BO-C$_2$H$_2$ and BS-C$_2$H$_2$ systems, we found both reaction systems share similarities but also striking differences. Both systems follow indirect reaction dynamics initiated by the barrierless addition of the radical reactant with its boron atom

Scheme 3. Potential Organo Sulfidoborons Formed in the Bimolecular Gas Reactions of Boron Monosulfide with Distinct Unsaturated Hydrocarbons (left) as well as the Products Formed in the Reactions of Boron Monoxide with the Same Hydrocarbons (right)
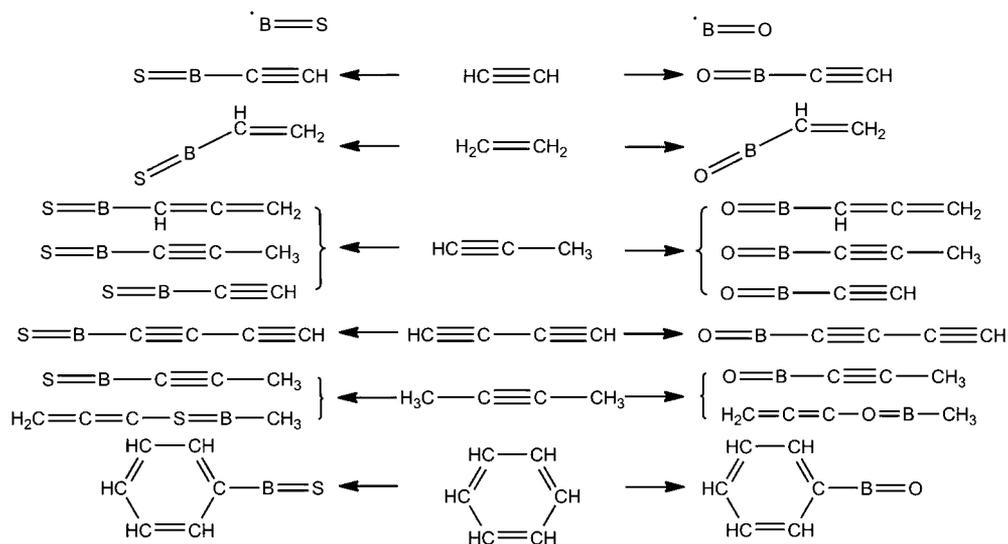
to the acetylene molecule followed by isomerization and atomic hydrogen losses to form the linear HCCBO and HCCBS products, respectively. Further, both systems possess similar geometrical constraints that the decomposing intermediates emit hydrogen atoms with a preferred direction of the atomic hydrogen loss, which is close to parallel to the total angular momentum vector and nearly perpendicular to the rotational plane of the decomposing intermediates. Referring to the potential energy surfaces, both systems have similar *cis/trans* double potential energy wells as their barrierless addition intermediates, and both of the *cis*-intermediates will rearrange via 1,2-hydrogen atom migration to the intermediates (H_2CCBO and H_2CCBS) of similar structures that possess the global potential minima in the respective reaction system. However, $BO-C_2H_2$ and $BS-C_2H_2$ systems exhibit striking discrepancies. In the $BS-C_2H_2$ system, *cis*-HCCHBS not only decomposes to the linear product HCCBS via a hydrogen atom emission but also undergoes a hydrogen atom migration from the C1 carbon atom of the acetylene moiety to the boron atom, which further decomposes to HCCBS via hydrogen atom emission from the boron atom. The similarity of the latter pathway is not found in the $BO-C_2H_2$ system. This feature is likely related to the polar triple bond character of the boron–sulfur bond. A dative π-bond by donation of one of the lone electron pairs from the sulfur atom to boron atom makes the boron atom more accessible to accept a migrated hydrogen atom from the neighboring carbon atom; this will result in a dramatic change of the branching ratios leading to the final products. From the RRKM studies, the branching ratios to the final products HCCBO plus hydrogen via *cis*-HCCHBO and H_2CCBO are 96% and 4% in the $BO-C_2H_2$ system, while the branching ratios to the final products HCCBS plus hydrogen via *cis*-HCCHBS (i2), H_2CCBS (i3), and HCCBHS (i4) are 21%, 7%, and 72% in the $BS-C_2H_2$ system, respectively. Therefore, upon reaction with acetylene, both the boron monosulfide radical and the isovalent boron monoxide radical hold similar reaction mechanisms such as indirect reaction dynamics, sideways scattering, and similar reaction intermediates and pathways leading to the linear products HCCBO and HCCBS but also present discrepancies due to the difference in

the chemical bonding of the reactant radicals that will dramatically change the branching ratios of the pathways leading to the respective final product system.

4. CONCLUSION

We have established the directed formation of a member of the organo sulfidoboron (RBS) family under single collision conditions in the gas phase via a bimolecular reaction exploiting the crossed molecular beams technique: the linear ethynylsulfidoboron molecule (HCCBS). Compared to the boron−sulfur bond distance of 160.9 pm,[37] the boron−sulfur bond in ethynylsulfidoboron is only slightly extended to 161.0 pm thus essentially keeping its triple bond character. The facile route to form an organo sulfidoboron molecule via the reaction of the boron monosulfide radical with an unsaturated hydrocarbon molecule can be considered as a benchmark study to form even more complexes, hitherto elusive organo sulfidoborons in the gas phase via directed formation. Considering the similarities of the reaction mechanisms of the isovalent BS−C_2H_2 and BO−C_2H_2 systems as discussed above, our findings let us predict that hitherto elusive organo sulfidoborons can be formed via bimolecular gas-phase reactions of the boron monosulfide radical with unsaturated hydrocarbons (Scheme 3), thus opening up an unconventional path to access the previously obscure class of organo sulfidoboron molecules, which are difficult to form through "classical" formation. It is clear that further experimental and theoretical studies of these systems under single collision conditions are warranted to fully expose the unique reactivity of the boron monosulfide radicals and the formation of the new class of organo sulfidoboron molecules. This might be also of potential interest to organometallic chemists by expanding the formation of BS⁻ coordinated Au(I) complexes such as $Au(BS)_2^-$, which is considered as a new candidate in gold-assisted catalytic chemistry, to Au(BS)(RBS).[38]

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Notes
The authors declare no competing financial interest.

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