Elementary Reactions of Boron Atoms with Hydrocarbons—Toward the Formation of Organo-Boron Compounds

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1. Introduction

The chemical reactivity of atomic boron, $B(^2P_j)$, with inorganic and organic molecules is a fascinating subject of research from the experimental[1−35] and theoretical viewpoints.[29,30,36−46] Atomic boron resides in the same row as carbon, nitrogen, and oxygen.[47] Although the reaction dynamics and kinetics of the latter elements (C, N, O) have been studied in depth,[48−53] an investigation of elementary reactions of boron atoms has remained sketchy so far. These studies are of significant interest due to the position of boron between metals and nonmetals. Apart from the fundamental importance of the elementary boron reactions,[54,55] bimolecular collisions involving atomic boron are relevant to material sciences[56] such as boron assisted nanotube growth[57] and the production of boron-doped diamond thin films,[58,59] chemical vapor deposition (CVD), high temperature combustion processes,[60,61] interstellar chemistry,[62] and the synthesis of novel organo-boron molecules.[39−41,45,46,63−69]

1.1. Organo-Boron Molecules in Combustion Systems

Due to its high energy density, in both volume and gravity terms, boron has long been regarded as a good candidate for rocket fuel additives.[70−78] To fulfill this potential, it is essential to understand the boron combustion chemistry and the reactions of boron atoms with hydrocarbon fuel together with the combustion products on the molecular level.[79−81] In particular, elemental boron is appealing for use as an enhancing agent in combustion applications due to its high theoretical energy density.[60,61,71,72,82,83] This, coupled with a high energy of the combustion process and low-molecular-weight products, explains why boron is considered an attractive material for use in rocket propellants and explosives.[79] Remarkably, the lack of experimental data, particularly for high-temperature gas-phase and surface boron chemical kinetic parameters, has severely complicated the construction of realistic models for the combustion processes.[84−86] The main problem when facing the study of elementary reactions of boron is the difficulty of preparing a significant concentration of boron atoms, since the enthalpy of sublimation is quite

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high $(565 \pm 5 \text{ kJ} \cdot \text{mol}^{-1})$.[87] The experimental studies on the kinetics of boron atom reactions available until 1995 were reviewed about one decade ago.[60] An inspection of those studies shows that the reaction rate constants were known for a very limited number of reactions with oxygen- and halogen-containing molecules.[88−95] However, reactions of boron atoms with organic molecules, in particular hydrocarbons, have not been reviewed to date.

1.2. Organo-Boron Molecules on Chemical Vapor Deposition and Material Sciences

Besides combustion settings, the reactivity of boron is also important to understand the underlying reaction mechanisms involved in chemical vapor deposition (CVD) processes.[96−99] Processes involving diborane, hydrogen, and simple hydrocarbons, in which atomic boron often prevails as a transient reactant, are important to manufacture boron-doped diamond films (p-type semiconductors, unconventional superconductor,[100] UV Schottky photodiodes)[57−59,101−103] and boron-doped hydrogenated amorphous carbon films via surface-wave mode microwave plasma CVD (applications to photovoltaic cells).[104−108] Here, electron-deficient bonding is a common feature in boron-rich solids, which would make it a logical choice for use in semiconductors[76,109] and possibly superconductors.[110,111] One set of semiconductors, which are currently of interest, are the boron carbides.[112,113] They are very stable, possess high electrical as well as low thermal conductivities, and have been considered as the most promising materials for realizing high-efficiency thermoelectric energy conversion given n-type boron carbides.[114] These materials have important applications as high-temperature semiconductors[107] and superconductors.[100,110] Also, boron-doped diamonds,[101,102] diamond films,[115,116] and boron-doped graphene layers[117] generated interest due to their applications in electron emission sources[118−120] and peptide microarrays.[74] Finally, amorphous BC_4N materials have been applied as protective coatings on hard steel substrates.[121] The related cubic BC_2N material was found to rank second among the superhard materials instead of cubic boron nitride (BN).[122] This research area relates well to the B_xH_y material, which forms superhard fibers via microvortex-flow hyperbaric laser chemical vapor deposition.[123]

1.3. Organo-Boron Molecules in Weakly Ionized Plasmas

Atomic boron reactions are further of interest to understand the chemistry in weakly ionized plasmas. Recall that atomic boron is isoelectronic with singly ionized carbon atoms, $C^+(^2P_j)$. Since singly ionized carbon atoms are abundant in weakly ionized plasmas with implications to etching and combustion processes,[124−126] an experimental investigation of the isoelectronic boron-analog reactions and access of the potential energy surfaces also help to rationalize the chemistry occurring in these environments—in particular the involvement of carbon cations in the formation of polycyclic aromatic like molecules, carbon nanotubes, nanoribbons, superhard fibers, and heterobucky balls.[46,57,61,117,127−133]

1.4. Organo-Boron Molecules in Astrochemistry

Finally, we would like to note that atomic boron has also 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).[62,134−136] 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.

1.5. Generalized Approach

An understanding of the chemical changes and evolution of boron reactions in combustion systems, CVD processes, material sciences, weakly ionized plasmas, and even in astrochemistry requires an incorporation of elementary boron reactions into pertinent chemical reaction models. These models suggest that the synthesis of small boron-bearing molecules together with their radicals is linked to the formation of composite, hydrogenated boron−carbon species. Various mechanisms have been postulated; those currently in favor are thought to involve a successive buildup of hydrogen-deficient boron- and carbon-bearing radicals and molecules. Here, particular attention has been devoted to understand the reactions of boron atoms with small carbon-bearing molecules. These processes were suggested to convert unsaturated hydrocarbons to larger, boron-bearing and hydrogen deficient hydrocarbon radicals.[137,138] Four kinds of data are crucial to obtain a legitimate and realistic picture of the formation of boron-bearing molecules and their precursors: (i) data on enthalpies of formation of important reaction products, (ii) detailed data on the reaction intermediates of bimolecular boron reactions, which can be stabilized and/or undergo further reactions in high pressure settings, (iii) the actual reaction products under single collision conditions, and (iv) basic information on the collision-energy dependent chemical dynamics. All these data are needed by modelers simulating the effects of pressure, temperature, and chemical composition in ignition and combustion systems, as found, for instance, in gas turbines, ramjets, scramjets, pulsed detonation engines, and chemical rockets. These studies also provide a solid scientific background for current and future applications of ceramics, ceramic-matrix composites (CMCs), and carbon-based composites in hypersonic aircrafts and space structures.

Since the majority of the reactions of boron atoms with hydrocarbons have not been comprehensively summarized for almost 15 years,[60] this review provides a thorough compilation of the gas phase kinetics of boron atoms with organic molecules (predominantly with hydrocarbons); these investigations obtain rate constants of bimolecular reactions involving boron atoms to determine how "fast" (or slow) a reaction proceeds (sections 2.1 and 3.1). Hereafter, matrix isolation studies of suprathermal, laser ablated boron atoms with hydrocarbon molecules are reviewed (sections 2.2 and 3.2). These experiments provide important information on reaction intermediates and—if the intermediates have sufficient excess energy in the matrix—on their decomposition products. Both intermediates and products can be probed spectroscopically in these cryogenic matrices via infrared spectroscopy. The final sections (2.3 and 3.3) summarize recent developments in the study of gas phase reactions of boron atoms under single collision conditions utilizing the crossed beam method. This experimental technique provides information on reaction products, their branching ratios, the intermediates involved, and the thermodynamic properties of product isomers—data which kinetic measurements do not commonly supply—at the molecular level without the interference of wall or matrix effects. Since all chemical processes in, for instance, combustion flames and CVD settings consist of multiple elementary reactions that are in principle a series of bimolecular encounters, crossed beam experiments represent a powerful approach to provide detailed knowledge of the elementary processes involved at the most fundamental, microscopic level.

2. Experimental Approaches

2.1. Kinetic Studies of Boron Atom Reactions

The available literature on the rate constants of gas phase atomic boron reactions with hydrocarbon molecules is particularly poor. Only a few kinetic investigations have been performed. Such a lack of studies is probably due to an intrinsic difficulty in generating boron atoms and a protracted underrating of the relevance of atomic boron gas phase reactions.[139] This situation is particularly striking if compared to the case of gas phase reactions involving other nonmetal atoms of the second period of the periodic table, such as carbon, nitrogen, oxygen, and fluorine, for which extensive studies have been reported over more than 40 years.[48,49]

An early interest in the gas phase kinetics of boron reactions has actually arisen as a consequence of the potential exploitation of boron-containing fuels. In particular, because of the high exoergicity of the formation of boron monoxide (BO), this led to the investigations of some reactions involving atomic boron and oxygen containing molecules, such as molecular oxygen (O_2) and water (H_2O).[88−91,93,140−143] Those results have already been reviewed by Bauer in 1996;[60] no other data have become available in the meantime on the kinetics of these systems. Since the focus of this review is on boron reactions with hydrocarbons leading to organo-boron compounds, it is worth noting that some reactions investigated by Davidovits and co-workers involved substituted organic compounds, such as alcohols,[91] epoxides,[93,141] and halocarbons.[92,94] The reaction with methane was also considered in the study of the substituted halocarbon series, but the boron plus methane system did not show any reactivity (the estimated upper limit for the 300 K rate constant was less than 4.0×10^{-15} cm^3 s^{-1} at 300 K).[92] In some reactions involving complex alcohols, ethers, and epoxides, it is conceivable that, in addition to the boron monoxide formation channel, alternative channels leading to organo-boron products could be possible. Some of these results will therefore be commented on here, so that a brief description of the experimental setup is in order. A schematic view of the apparatus employed by Davidovits and co-workers is given in Figure 1.[92] Here, the boron atoms were produced in a microwave discharge of a dilute mixture of diborane (B_2H_6) in rare gases.[88−93,141] The reactants were injected into the flow tube through a multiholed Teflon loop system; the density of boron atoms was monitored by absorption of the 249.773 nm boron atom resonance line at five optical windows placed along the flow tube.[88−93,141] That means that in those experiments only the boron atom disappearance rate was actually measured. For several reactive systems, a parallel gas beam apparatus was also utilized to monitor the chemiluminescence of the first
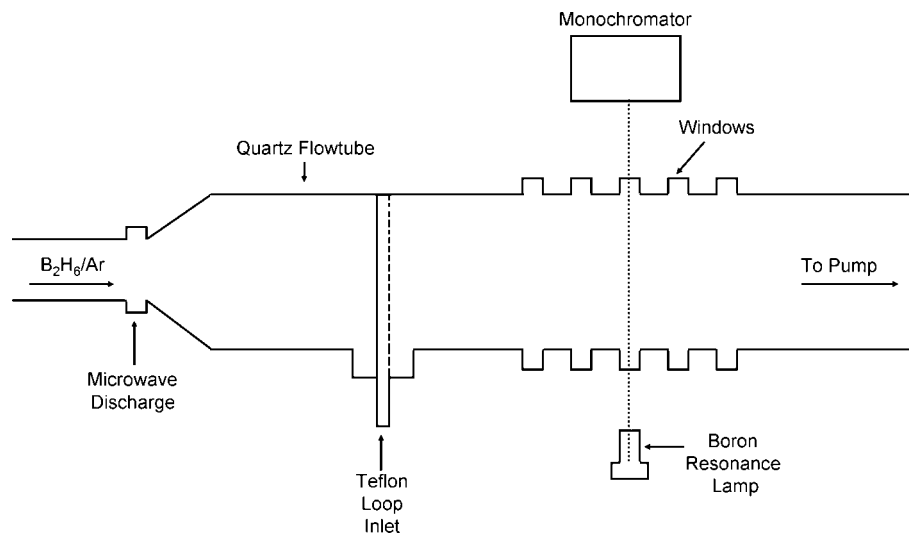
Figure 1. Schematic experimental setup of the flow tube apparatus used in kinetic study of the atomic boron−methane system. Reprinted with permission from ref 92. Copyright 1985 American Institute of Physics.
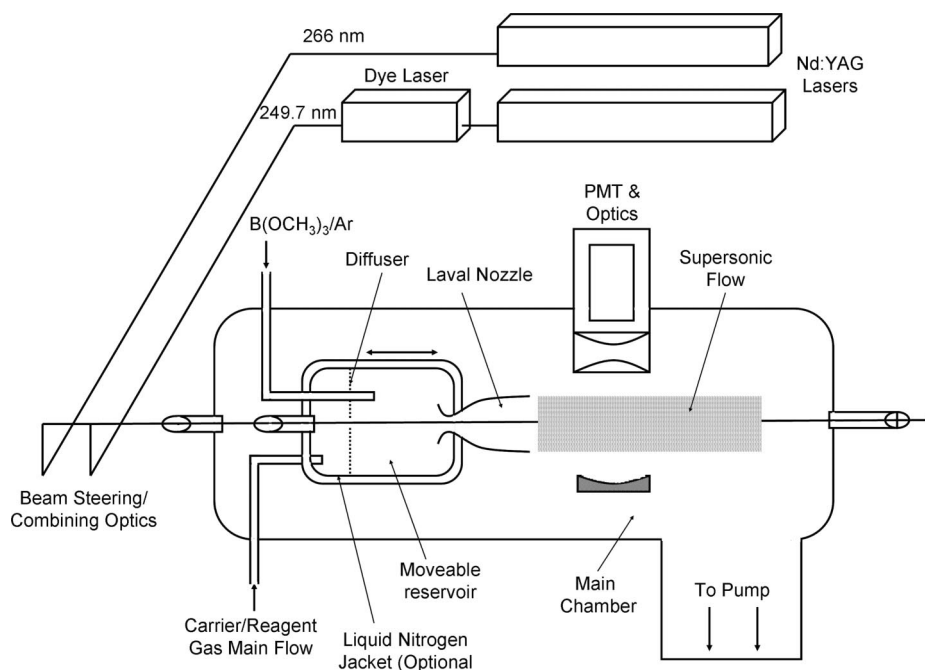

Figure 2. Schematic experimental setup of the CRESU apparatus used in the kinetic studies of the boron−acetylene and boron−ethylene systems. Reprinted with permission from ref 144. Copyright 1994 American Institute of Physics.

electronically excited $A^2\Pi$ state of boron monoxide under single collision conditions.[142,143] In those cases, boron vapors were generated by electron bombardment heating of solid boron in a graphite lined tantalum crucible heated to about 2300 K. The BO($A^2\Pi$) chemiluminescence was detected by a spectrometer-photomultiplier-pulse counting system.[142,143] The formation of BO($A^2\Pi$) was indeed observed not only in the case of the B + O_2 system but also in the cases of reactions of boron with epoxides.[143] In this way some interesting information on the nature of the primary products and the mechanism of reaction was obtained.

After this first series of experiments, almost 20 years passed before new kinetic data became available. This is in spite of the renewed interest in the gas phase reactions of boron atoms for their role in material sciences, especially as far as boron assisted nanotube growth and boron-doped diamond thin films production are concerned. A consequence of the lack of kinetic data on the reactions of boron atoms

with the relevant hydrocarbons is that the modeling of those systems is rather incomplete.[84−86,104] The new data concerned the reactions between atomic boron with acetylene[6] and ethylene,[35] which have been investigated by means of the CRESU (the acronym for the French *Cinetique Supersonique de Reaction en Ecoulement Uniforme*) technique in the range of temperature between 25−295 K. This sophisticated technique has been specifically optimized to the study of bimolecular reactions at very low temperatures, as the expansion of a gas mixture through an axisymmetric, converging-diverging Laval nozzle, leads to the production of a cold and uniform supersonic flow of gas (see Figure 2).[144,145] This expansion forms a relatively dense medium ($10^{16}-10^{17}$ cm^{-3}) in which the temperature and number density are constant along the axis of the flow over a few tens of centimeters. Different nozzles and carrier gases are used to produce a specific flow temperature; the supersonic flow regime is maintained as such also when 1−2% of

additional gases are added. The chemically unstable reactant in the gas mixture (generally an atomic or radical species, but also unstable closed-shell molecules such as dicarbon) is generated via pulsed laser photolysis of an appropriate molecular precursor. In the case of the two reactions illustrated here, the boron atoms were generated by UV multiphoton photolysis of trimethylborate $(B(OCH_3)_3)$.[6,35] The boron atom density was monitored downstream at a certain distance from the photolysis focal region by laser-induced fluorescence. The $2s^22p\ ^2P_{1/2} \leftarrow 2s^23s\ ^2S_{1/2}$ and $2s^22p\ ^2P_{3/2} \leftarrow 2s^23s\ ^2S_{1/2}$ resonance transitions at 249.677 and 249.772 nm were used. The evolution of the laser induced fluorescence (LIF) intensities for both transitions at various detection distances confirmed that the thermodynamic equilibrium at the temperature of the flow was achieved for the two spin—orbit levels ($^2P_{1/2}$ and $^2P_{3/2}$) in a short time compared to the reaction. One limit of the CRESU technique is that the supersonic flow is uniform only over distances of a few tens of centimeters; that is, the change of concentration of the atom/radical reactant has to occur in a time scale of $100-500\ \mu$s. Therefore, this technique cannot be employed to study reactions with room temperature rate constants smaller than $10^{-12}\ cm^3\ s^{-1}$. This limitation is serious in the case of the reactions between boron and saturated hydrocarbons such as methane, because they are predicted to have an activation energy (see below) and, therefore, they are not fast. Another limit is that the temperature that can be attained does not exceed room temperature. The low temperature range is very interesting when one is concerned with low temperature environments such as planetary atmospheres and interstellar clouds chemistry—the topic within which the CRESU technique has gained its fame. It is also true that the data obtained at very low temperatures are quite sensitive to the details of the potential energy surface which describes the reactive system. Nevertheless, since the potential applications of boron plus hydrocarbon reactive systems deal with high temperature environments such as chemical vapor deposition, the low temperature kinetic data might not be representative of the boron chemistry in those cases, since different reaction pathways could be open at higher temperatures. Note that the CRESU study on the boron plus acetylene system has been accompanied by a crossed beam

Figure 3. Schematic experimental setup of the crossed beams apparatus used in the boron —acetylene study by Naulin and Costes (PV1 and PV2, pulsed valves for the boron atom beam and the acetylene molecular beam; ALB, ablation laser beam; PLB, probe laser; PMT, photomultiplier tube). Reprinted with permission from ref 155. Copyright 1999 Elsevier.

experiment in which the integral cross section as a function of collision energy was determined for the isotopic variant of D2-acetylene C_2D_2 (section 3.3). A schematic of the crossed beam machine employed is given in Figure 3. In that experiment, the boron beam was produced by laser ablation of a solid boron rod. The deuterium atom detection was achieved by one-photon resonant LIF using the Lyman-α transition at 121.534 nm.

2.2. Matrix Isolation Studies of Atomic Boron Reactions

The technique of matrix isolation coupled with laser ablation of refractory material has been widely used to produce and trap new species which have been characterized by electron spin resonance (ESR) or by infrared (IR) spectroscopy.[146,147] The advantage of this method is that the solid refractory material, such as solid boron itself, can be easily ablated by a high-energy laser pulse. In principle, it is feasible to produce essentially atomic species, since the large excess energy of the laser pulse breaks apart any possible cluster of atoms via multiphoton dissociation. The low temperature condensation of the atomic species with a reactive gaseous partner, in the presence of a large excess of an inert and spectroscopically transparent gas, allows isolating the interacting species. The basics of the technique have been described in previous reviews.[146,147]

Of relevance to the present review are the matrix studies of several reactions of laser ablated boron atoms with hydrocarbons (namely methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), and ethane (C_2H_6)) that have been used to produce and characterize new small organo-boron species via infrared spectroscopy.[7,11–16,148] Other carbon containing species have also been synthesized in matrix experiments, including the CBC radical[38] and organo-boron compounds containing fluorine (F), chlorine (Cl), bromine (Br), sulfur (S), nitrogen (N), and oxygen (O).[22–25,149] These matrix studies were complemented by theoretical vibrational spectra, thus allowing the assignment of the observed infrared bands after taking into consideration scaling factors to account for the anharmonic nature of the molecular vibrations compared to the computed harmonic approach. In addition to the characterization of previously unknown species, those studies have paved the way to the understanding of the rich chemical behavior of boron atoms. About this last point, however, it is important to remember that, when comparing reactions occurring in a collision-free gas phase experiment with a matrix experiment, there are important differences that should be kept in mind. As a matter of fact, the reactive intermediates or primary products which are formed by a reaction, both in the gas phase at low pressure or in an inert matrix at low temperature, are isolated, and with an appropriate method of interrogation, therefore, both sets of conditions offer the opportunity to characterize those species as they are formed in bimolecular collisions. Nevertheless, the matrix environment is able to disperse the energy released by an exoergic reactive encounter, which is normally channelled into translational or internal energy of reaction intermediates and/or products. If a bound intermediate is formed during the reaction in a collision-free gas-phase environment, the excess internal energy induces a bond fission, so leading to the formation of products. The products are then formed with a certain amount of translational energy, which guarantees that the two (or more) moieties separate the one from each other (they "fly apart") without further reciprocal interactions. On
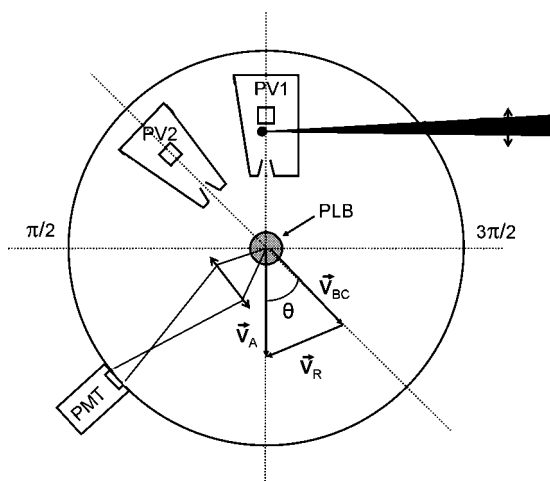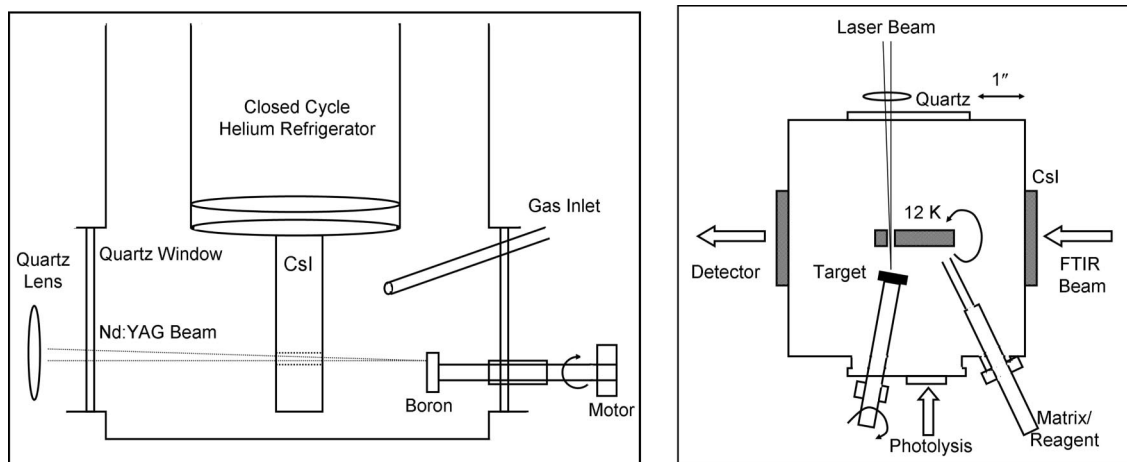
Figure 4. Schematic experimental setup of the matrix FTIR machine; the right figure presents the horizontal view. Reprinted with permission from ref 150 (Copyright 1991 American Institute of Physics) and ref 151 (Copyright 1992 American Chemical Society).

the contrary, when a bound intermediate is formed as the initial step of a bimolecular reaction, the matrix environment can stabilize the intermediate. Also, when the products are formed by the fragmentation of the intermediate, the difficulty with which the two products separate within the matrix is such that they might find their way to recombine and form the same or another bound species, which, in turn, can be stabilized by the matrix. In a direct reaction that does not proceed through the formation of a bound intermediate, the products can still experience some difficulties in separating the one from each other because of the matrix and recombine or form another set of products. In summary, the matrix cage effect might profoundly influence the outcome of a bimolecular reactive collision and, therefore, the information obtained in this respect, though valuable, should be regarded with caution. The apparatus used for the study of the boron interaction with hydrocarbons has been described in the relevant paper. A simplified scheme is given in Figure 4.[150,151] Briefly, the apparatus consisted of a closed-cycle helium refrigerator, a vacuum chamber, and a pulsed neodymium−yttrium aluminum garnet (Nd:YAG) laser. A piece of boron was epoxy glued to the end of a glass rod and rotated at 1 rpm, and the fundamental of the YAG laser beam was focused by a 10 cm focal length quartz lens onto the target. With approximately 20−40 mJ per pulse of laser power at the boron target, the boron atom concentration in the argon matrix was on the order of 0.1%; however, the spin state of the boron atoms was not characterized. The ablated boron atoms were codeposited with a mixture of argon (0.1−0.5%) hydrocarbon. The infrared spectra were collected before and after medium pressure mercury arc photolysis and annealing.

2.3. Dynamics Studies of Atomic Boron Reactions

Which experimental approach can reveal the chemical dynamics of ground state boron atom reactions with hydrocarbons? Since the macroscopic chemical evolution of, for instance, boron combustion and boron chemical vapor deposition processes involves multiple elementary reactions, which can be considered as a series of *bimolecular encounters*, a detailed understanding of the underlying reaction mechanisms at the most fundamental, microscopic level is desirable. These are experiments under *single collision conditions*, in which particles of one supersonic beam, here

ground state boron atoms, are made to "collide" *only* with particles of a second beam, i.e. the hydrocarbon reactant. The crossed molecular beam technique represents the most versatile approach in the elucidation of the energetics and dynamics of elementary reactions.[49,152−154] In contrast to bulk experiments, where reactants are mixed, the crossed beam approach has the capability of producing the boron atoms and the hydrocarbon reactants in separate supersonic beams. In principle, both reactant beams can be prepared in well-defined quantum states before they cross at a specified energy under well-defined single collision conditions; these data help to derive, for instance, the reaction mechanism, entrance barriers, information on the reaction intermediates, and product distributions under the absence of wall effects. These features provide an unprecedented opportunity to observe the consequences of a single collision event, excluding secondary collisions. The products of bimolecular reactions can be detected via spectroscopic detection schemes such as laser induced fluorescence (LIF)[155,156] or Rydberg tagging,[157] via ion imaging probes,[158−162] or via a quadrupole mass spectrometric detector (QMS) with universal electron impact ionization or photoionization. Crossed beam experiments can therefore help to untangle the chemical dynamics and infer the intermediates and the nascent reaction products *under single collision conditions.*

The use of crossed molecular beams has led to an unprecedented advancement in our understanding of fundamental principles underlying chemical reactivity in light elementary reactions such as tri-[163−177] and tetra-atomic systems.[178−180] These simple systems are prototypical reactions in bridging our theoretical understanding of reactive scattering, via dynamics calculations on chemically accurate potential energy surfaces, with experimental observations.[181] These dynamics calculations are needed to turn the *ab initio* results into quantities that can be compared with experiments. Although interest in these light elementary reactions still continues, with the development of powerful theoretical models, attention is turning to more complex systems of significant practical interest such as in catalysis,[182−189] atmospheric chemistry,[190−192] interstellar[193−205] and planetary chemistry,[206−211] organometallic chemistry,[5,6,212] and combustion processes.[213−218] Due to the experimental difficulties in generating atomic boron atoms in supersonic beams, only a very few atomic boron−hydrocarbon reactions have been conducted so far under single collision conditions. In a series

of experiments using a crossed beam machine with a rotating QMS detector, the differential cross sections for the reactions involving atomic boron and acetylene, ethylene, methylacetylene, allene, dimethylacetylene, and benzene have been determined (section 3.3). In addition, the integral cross section as a function of the collision energy has been measured for the reaction of boron with D2-acetylene by means of a crossed beam machine with a rotating source and deuterium atom detection achieved by one-photon resonant Lyman-α LIF.

2.3.1. Crossed Beam Machines with a Rotating QMS Detector

The differential cross sections for the reactions $B + C_2H_4$, $B + C_2H_2$, $B + C_3H_4$ (methylacetylene and allene), $B + CH_3CCCH_3$, and $B + C_6H_6$ have been characterized by using a crossed molecular beam apparatus with a "universal" detection scheme. The machine consists of two source chambers at a crossing angle of 90°, a stainless steel scattering chamber, and an ultrahigh-vacuum tight, rotatable, differentially pumped quadrupole mass spectrometric (QMS) detector which can be pumped down to a vacuum in the high 10^{-13} Torr range (Figure 5). In the primary source, a *pulsed* beam of ground state boron atoms is generated via laser ablation of boron rods.[219] The pulsed primary beam is passed through a skimmer into the main chamber; a chopper wheel located after the skimmer and prior to the collision center selects a slice of species with well-defined velocity which reaches the interaction region. Typical beam velocities of 800 ms^{-1} to 2950 ms^{-1} can be obtained. This section of the beam intersects then a pulsed reactant beam released by a second pulsed valve under well-defined collision energies. Crossed beam experiments utilizing pulsed beams allow experimental studies with often expensive (partially) deuterated chemicals to extract additional information on the

reaction dynamics, such as the position of the hydrogen and/ or deuterium loss if multiple reaction pathways are involved. In addition, pulsed sources with high beam densities allow that the pumping speed and hence costs can be reduced drastically. To detect the product(s), the crossed beam machine incorporates a triply differentially pumped, universal quadrupole mass spectrometric detector coupled to an electron impact ionizer. Here, any reactively scattered species from the collision center after a single collision event has taken place can be ionized in the electron impact ionizer, and—in principle—it is possible to determine the mass (and the gross formula) of all the products of a bimolecular reaction by varying the mass-to-charge ratio, *m/z*, in the mass filter. Since the detector is rotatable within the plane defined by both beams, this detector makes it possible to map out the angular and velocity distributions of the scattered products in the laboratory reference frame. Measuring the time-of-flight (TOF) of the products, i.e. selecting a constant mass-to-charge value in the controller and measuring the flight time of the ionized species, from the interaction region over a finite flight distance at different laboratory angles allows extracting the product translational energy and angular distributions in the center-of-mass reference frame. This provides insight into the nature of the chemical reaction (direct vs indirect), the intermediates involved, the reaction product(s), their branching ratios, and in some cases the preferential rotational axis of the fragmenting complex(es) and the disposal of excess energy into the products' internal degrees of freedom as a function of scattering angle and collision energy. However, despite the triply differential pumping setup of the detector chambers, molecules desorbing from wall surfaces lying on a straight line to the electron impact ionizer cannot be avoided. Their mean free path is of the order of 10^3 m compared to maximum dimensions of the detector chamber of about 1 m. To reduce this background, a copper plate attached to a two-stage closed cycle helium refrigerator is placed right before the collision center and cooled down to 4 K. In this way, the ionizer views a cooled surface which traps all species with the exception of hydrogen and helium. The experimental observables contain basic information. Since every species can be ionized at the typical electron energy used in the ionizer, it is possible to identify the nature of the primary products. Even though some problems such as dissociative ionization and background noise limit the method, when the reaction products are unknown, the advantages of mass-spectrometric detection over spectroscopic techniques are obvious, since the applicability of the latter needs the knowledge of their optical properties. Another important aspect is that, by measuring the product velocity distributions, one can immediately derive the amount of the total energy available to the products and, therefore, the enthalpy of reaction of the reactive collision. This is of great help when different structural isomers with different enthalpies of formation can be produced. For a more detailed physical interpretation of the reaction mechanism, it is necessary to transform the laboratory (LAB) data into the center-of-mass (CM) system using a forward-convolution routine.[220] This approach initially assumed an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution were then calculated from these center-of-mass functions. The essential output of this process is the generation of a product flux contour map. This function reports the flux of the reactively scattered
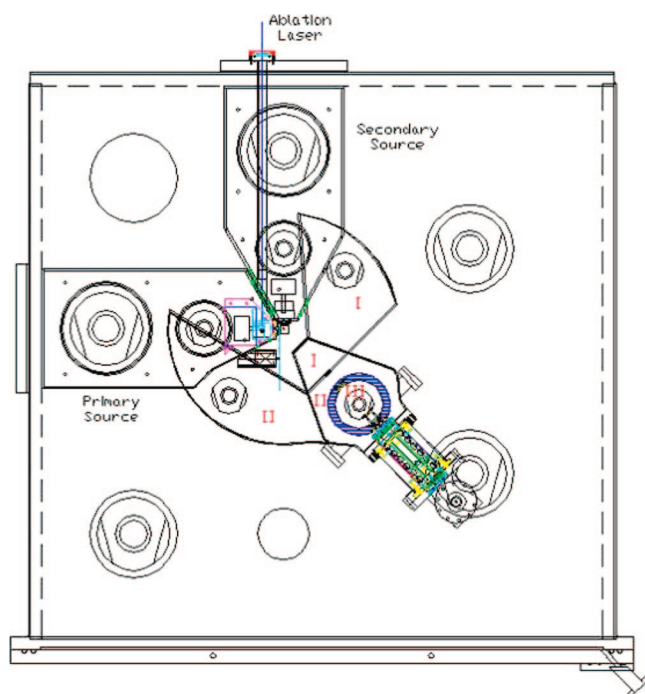

Figure 5. Top view of the crossed molecular beams machine utilized in the dynamics studies of boron atom reactions with unsaturated hydrocarbons. The ablation source is located in the primary source chamber. Reprinted with permission from ref 213. Copyright 2006 The Royal Society of Chemistry.

products as a function of the center-of-mass scattering angle and product velocity and is called the reactive *differential cross section*. This map can be seen as the *image* of the chemical reaction and contains *all* the information on the scattering process. For completeness, it should be mentioned that if the spectroscopic properties of the products are known, state-to-state differential cross sections can be obtained, for example, with the use of REMPI and velocity map imaging; this would not be possible with a mass spectrometer detector. Both techniques can yield valuable results, so the "universal detection" and spectroscopic detection tools are highly complementary.

2.3.2. Crossed Beam Machine with a Rotating Source

Figure 3 portrays a schematic top view of a crossed beam machine with a rotating molecular beam source (PV2) used to determine the integral cross section as a function of the collision energy (excitation function) for the reaction of boron atoms with D2-acetylene. During the experiment, the beam intersection angle was varied from 90.0° to 22.5°, thus allowing one to vary the collision energies in the range between 0.35 and 9.4 kJ mol^{-1}. So far, only the reaction of atomic boron with deuterated acetylene has been studied with this experimental approach (attempts to obtain a reactive signal with acetylene failed because of a spurious background signal in hydrogen atom spectroscopic detection). The supersonic boron beam was produced by laser ablation of a boron rod and seeding the ablated species into neon or argon carrier gas. In this setup, atomic hydrogen (deuterium)—the cofragment in the hydrogen atom displacement channel—was probed via laser-induced fluorescence (LIF). Briefly, the D($^2S_{1/2}$) atoms produced in the reaction were probed by one-photon resonant LIF using the ($^2P_j \leftrightarrow {}^2S_{1/2}$) Lyman$-\alpha$ transition at 121.534 nm and a photomultiplier tube as a detector. The vacuum ultraviolet photons were generated by frequency tripling UV radiation around 365 nm in krypton gas. The VUV beam propagated perpendicular to the molecular beam scattering plane, that is perpendicular to the relative velocity vector. Relative, collision energy-dependent cross sections of the D atom yields were obtained by dividing the averaged signal intensities by the relative velocities of the reactants.

3. Results

3.1. Kinetic Studies of Boron Atom Reactions

3.1.1. Oxygen-Containing Organic Molecules

In the kinetic investigations of the reactions of boron atoms with oxygen containing organic molecules by Davidovits and co-workers, only the boron atom disappearance rate was followed.[88−91,93,141] Nevertheless, the reaction mechanisms were speculated on by investigating a series of chemically similar reactants and analyzing the trend of the rate constants with several aspects such as the length of the carbon chain, the type of carbon (primary, secondary, or tertiary) to which the oxygen atom is bound, and the presence of a π-bond or of a halogen substituent. For instance, in the series of studies involving alcohols and ethers, the rate constants were essentially the same (and in the range of 10^{-10} cm^3 s^{-1}) from methanol to *tert*-butyl alcohol and from allyl alcohol to furan.[91] These findings are quite interesting and might point to a direct interaction of the boron atom with the oxygen of

the molecule. Such an interaction appears to be not affected by the rest of the molecule. In light of the new results on the reaction of boron atoms with unsaturated acetylene (C$_2$H$_2$)[6] and ethylene (C$_2$H$_4$)[35] (see below), those results are even more remarkable, as the boron atoms are now known to interact easily and without appreciable barriers with unsaturated π-bonds. This could imply that, in the case of allyl alcohol or furan, other sites should be available to interact with the electrophilic boron atoms in these Lewis acid (boron atom)−Lewis base (alcohol) reactions. The situation is more ambiguous in the case of the reactions between boron atoms and a series of epoxides. The largest reaction rates were those measured for propylene oxide and epoxybutane. Adding another epoxy group, as in the case of the reaction with butadiene diepoxide, did not accelerate the rate constant, which is actually smaller [(5.5 ± 2.2) × 10^{-11} cm^3 s^{-1}] than that of the reaction of boron with propylene oxide [(8.6 ± 3.4) × 10^{-11} cm^3 s^{-1}]. Also, the presence of one or more chlorine atoms, such as in the case of the reactions of boron with epichlorohydrin and 1,2-epoxy-3,3,3-trichloropropane inhibits rather than enhances the reaction rate.[92] Yet, there is not a clear trend in the series of reactions of boron with ethylene dioxide, propylene oxide, epoxybutane, and styrene oxide. The rate constant for the boron−styrene oxide is larger than that for the boron−ethylene oxide system but smaller than that for reactions with propylene oxide and epoxybutane. One could expect that, in the case of the reactions involving epoxides with a carbon−carbon double bond such as butadiene monoxide and vinyl-oxabicycloheptane or an aromatic ring such as styrene oxide, an electrophilic interaction of boron atoms with the π-system of olefins and aromatic rings is a possible reaction pathway. Nevertheless, an investigation of the values of the room temperature rate constants of the boron epoxides series[93] shows no obvious trend in the reactivity when moving from saturated epoxides to unsaturated ones; the fastest reactions are those involving propylene oxide and epoxybutane. In the complementary chemiluminscence studies, the formation of boron monoxide in the electronically excited A$^2\Pi$ state was actually documented in the case of the reactions between boron atoms and epoxides. The intensity of the BO(A$^2\Pi$) emission was compared to the intensity observed for the boron−molecular oxygen reaction to estimate the BO(A$^2\Pi$) formation cross sections. The chemiluminscence cross sections for the reactions of boron atoms with epoxides were all about an order of magnitude smaller than that for the boron−molecular oxygen system, even though the exoergicity of the reactions of boron with epoxides leading to boron oxide and the corresponding species containing a carbon−carbon double bond is much larger (about 4.7 eV) than that associated with the boron−oxygen reaction (about 3.4 eV); also, an extra energy of ∼2.9 eV is required to reach the A$^2\Pi$ state. In addition, the room temperature rate constants for the boron plus epoxide reactions were systematically much larger than that for boron with oxygen. The reduced production of BO(A$^2\Pi$) was interpreted by assuming that, when a boron atom interacts with an epoxide molecule to extract an oxygen, a long-lived complex is formed, and a more efficient energy redistribution takes place. This could prevent the formation of BO(A$^2\Pi$). Nevertheless, an alternative explanation could be that the total cross sections are larger and the cross section to form BO(A$^2\Pi$) is smaller in the case of the reactions with the epoxides compared to molecular oxygen. Interestingly,

in the case of the reaction of boron with butadiene diepoxides, chemiluminiscence from boron dioxide (BO_2) was also observed; this suggests that a direct oxygen atom abstraction is not necessarily the only reactive channel, as in the case of the reactions with alcohols; recall that the authors implied that in all cases only a long-lived complex forming reaction mechanism can explain the reduced formation of $BO(A^2\Pi)$.

3.1.2. Hydrocarbon Molecules

In the kinetic investigations of the reactions of boron atoms with acetylene (C_2H_2)[6] and ethylene (C_2H_4)[35] involving the CRESU technique, the ground state boron atom disappearance rate was investigated in the temperature range of 23−295 K using different buffer gases and Laval nozzles. The rate constants for the reactions of boron atoms with acetylene[6] were found to be quite large, with a 295 K value of $(2.88 \pm 0.30) \times 10^{-10}$ cm^3 s^{-1}. At lower temperatures, the rate constants increase, with a slight negative temperature dependence up to 70 K, where the rate constant exhibits a maximum value; after this point, the rate constant starts decreasing. The experimental values of the rate constant as a function of temperature over the temperature range 23−295 K were fitted by the analytical expression (eq 1)

$$k(T) = (3.21 \times 10^{-10})(T/300)^{-0.5} \exp(-37/T) \text{ cm}^3 \text{ s}^{-1} \tag{1}$$

Similar values and similar trends were derived for the reaction of ground state boron atoms with ethylene.[35] At 295 K, the rate constant is close to the gas kinetic limit, being $(1.52 \pm 0.11) \times 10^{-10}$ cm^3 s^{-1}; there is a slight negative temperature dependence up to 70 K, where the rate constant reaches a maximum. The experimental values of the rate constant as a function of temperature over the temperature range 23−295 K were fitted by the analytical expression (eq 2).

$$k(T) = (1.86 \pm 0.40) \times 10^{-10}(T/300)^{-(0.70 \pm 0.30)}$$
$$\exp(-(26 \pm 14)/T) \text{ cm}^3 \text{ s}^{-1} \tag{2}$$

The presence of a maximum in the temperature dependence of the rate constant in CRESU experiments has already been derived for the reactions of silicon atoms with unsaturated hydrocarbons,[221] molecular oxygen, and nitrogen monoxide.[222] In the case of the reactions with molecular oxygen and nitrogen monoxide, the presence of a maximum in the

temperature dependence of the rate constants, however, was not related to the existence of a small entrance barrier. Rather, the adiabatic capture theory used to reproduce the temperature dependence of the reaction showed that the maximum could be related to the difference of reactivity of the spin−orbit states of the atom involved. Such an explanation can also hold for the reactions of boron with acetylene and ethylene. Because of the very fast collisional relaxation of the spin−orbit states $^2P_{1/2}$ and $^2P_{3/2}$ in the CRESU setup, it was not possible to perform kinetic experiments for each level of the boron atom electronic ground state in order to obtain state-to-state rate constants. Nevertheless, the CRESU experiment on the reaction between boron atoms and acetylene was complemented by a low kinetic energy crossed molecular beam experiment.[6] The trend of the derived excitation function for the isotopic variant utilizing D2-acetylene seems to be more in line with the presence of a very small reaction threshold of about 0.18 kJ mol^{-1}, possibly in the form of a barrier in the entrance channel of the potential energy surface.

3.2. Matrix Isolation Studies of Atomic Boron Reactions

Matrix isolation studies on the interaction of boron atoms with hydrocarbons focused on the reactions with methane (CH_4),[11−13,148] acetylene (C_2H_2),[7,14] ethylene (C_2H_4),[15,16] and ethane (C_2H_6).[16] The main results will be briefly summarized in the following sections.

3.2.1. Reaction with Methane (CH₄)

The most widely investigated B reaction in matrix experiments is that with methane.[11−13,148] Through the comparison with *ab initio* calculations combined with isotopic shifts and isotopic intensity distribution patterns (using ^{10}B, ^{13}C, and D),[11,13] the identification of several organo-boron species—never observed before—has been achieved (Figure 6). Considering the reaction mechanisms, it was suggested that atomic boron inserts into the carbon−hydrogen bond of methane, forming an internally excited insertion intermediate, CH_3BH (**i1**). The matrix-stabilized intermediate (**1**) species was tentatively identified via the analysis of the isotopic shifts related to the strong infrared band at 2561 cm^{-1}, corresponding to the boron−hydrogen stretching mode. The H_2CBH_2 species (**2**), which can be formed via a hydrogen shift in CH_3BH, was also identified through four infrared bands,
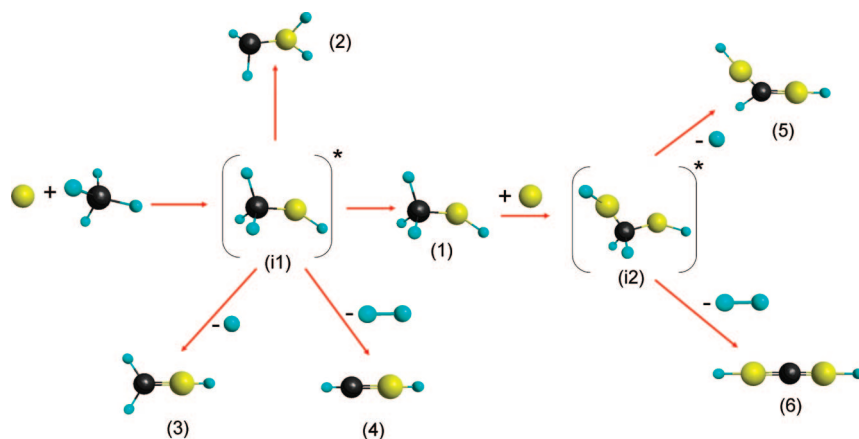

Figure 6. Proposed reaction mechanisms during the reaction of hyperthermal boron atoms with methane under matrix isolation conditions. Reprinted with permission from ref 12. Copyright 1993 American Chemical Society.

$\nu(BH_2) = 972.4$ (1073.3) cm^{-1}, $\nu(BH_2) = 1239.8$ (1328.6) cm^{-1}, $\nu(CH_2) = 1414.7$ (1582.9) cm^{-1}, and $\nu(BH_2) = 1239.8$ (1328.6) cm^{-1}, where the numbers in parentheses are the calculated values at the SCF/DZP level of theory. An atomic hydrogen elimination product, H$_2$C=BH (**3**), was also monitored with a B—H stretching mode at 2724.6 (2924.9) cm^{-1}, a C=B stretching mode at 1469.7(1506.6) cm^{-1}, and BH and CH$_2$ deformation modes at 902.6 (951.2), 705.7(741.4), and 611.8(634.8) cm^{-1}. Finally, a molecular hydrogen emission product, the HC=BH radical (**4**), was identified via a C—H antisymmetric stretching band at 3248.8(3554.4) cm^{-1}, a B—H stretching mode at 2743.4(2976.5) cm^{-1}, and a C=B stretching mode at 1475.3(1618.9) cm^{-1}. Other species observed result from secondary reaction of species **1** in the matrix with another boron atom via intermediate **i2**. In particular, a radical with the formula CH(BH)=BH (**5**) was believed to be responsible for the bands observed at 894.3 cm^{-1} (vibration of a BH subgroup), at 1137.3 cm^{-1} (C—B stretching halfway between single and double carbon—boron bond values), and at 2609.7 cm^{-1} (B—H stretching mode). Also, a species with two equivalent boron atoms and carbon—boron double bonds, HB=C=BH (**6**), was identified from a natural boron isotopic triplet at 1895.2 (2034.2; [10]B), 1883.9 (2022.2; [10,11]B), and 1872.0 (2009.6; [11]B) cm^{-1} associated with a BCB bond with two equivalent B atoms.[12] The methane parent molecule absorptions interfered with the antisymmetric BH stretching mode of HB=C=BH, and these bands were observed at 2213.1 (2380.8) cm^{-1} only in the experiment using CD$_4$. Based on the observation of the intermediates and products combined with *ab initio* calculations at CCSD (with ZPVE correction), the following reaction mechanism was suggested.[13] The reaction proceeds via insertion of the boron atom into one of the C—H bonds, leading to the CH$_3$BH intermediate (**i1**), which is formed with ~205 kJ mol^{-1} of internal energy. The excess of internal energy can be quenched by the matrix, so allowing the survival and detection of the CH$_3$BH radical (**1**). Alternatively, the insertion intermediate (**i1**) rearranges to H$_2$C—BH$_2$ (**2**), which is predicted to be more stable by 44 kJ mol^{-1}, or decomposes into products **3** and **4**. The thermochemistry of the dissociation pathways of CH$_3$BH to CH$_3$ + BH, CH$_3$B + H, and CH$_2$BH + H was characterized by *ab initio* calculations. Only the reaction channel leading to CH$_2$BH (**3**) plus atomic hydrogen is exoergic by 40.5 kJ mol^{-1} with respect to the reactant asymptote, but also the second, endoergic channel to form (**4**) plus molecular hydrogen might be open under the conditions of the matrix experiments because of the excess of energy associated with the hyperthermal boron atoms formed from laser ablation. Also the isomeric intermediate H$_2$C—BH$_2$ (**2**) may produce either H$_2$C=BH (**3**) via a hydrogen atom displacement channel or HC=BH (**4**) via molecular hydrogen elimination.[11–13]

3.2.2. Reaction with Acetylene (C$_2$H$_2$)

The second reaction of atomic boron with hydrocarbons, which received particular attention, was the boron—acetylene system[7,14] (Figure 7). Here, multiple novel organo-boron species have been identified in the matrix. Two spectral regions have led to the identification of the new species. The region around 2100—1900 cm^{-1} was associated with a species with strong C=C stretching modes, whereas the region around 1200—1100 cm^{-1} revealed product absorptions at 1175.3, 1170.6, and 1122.7 cm^{-1}. The 1170.6 cm^{-1} band was attributed via the isotopic shifts to the symmetric BC$_2$
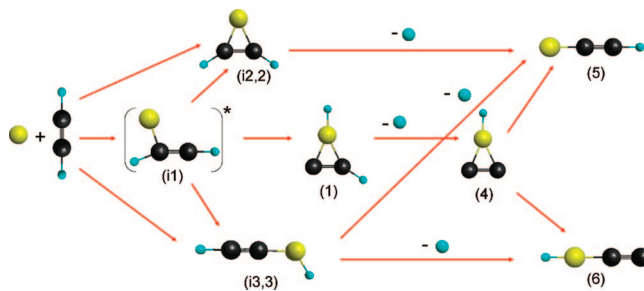

Figure 7. Proposed reaction mechanisms during the reaction of hyperthermal boron atoms with acetylene under matrix isolation conditions. Reprinted with permission from ref 7. Copyright 1993 American Chemical Society.

stretching vibration with two equivalent carbon atoms.[7] The assignment was confirmed by the calculations at the MP2 level (with the double-ζ plus polarization basis set), which also derived the structure of the cyclic borirene radical (**2**).[7] According to them, the C=C bond in BC$_2$H$_2$ is longer than that in C$_3$H$_4$, while the B—C bond is shorter than a typical single bond, so implying some delocalization of the two π electrons over the BC$_2$ ring having an aromatic character. The 1122.7 cm^{-1} band was instead assigned to the cyclic HBC$_2$ species (**4**), the calculated structure of which implies also an aromatic BC$_2$ ring. In a subsequent paper,[14] some isomeric forms of borirene radicals have also been characterized and identified in the infrared spectra through isotopic shifts, namely a bent HBCCH species (**3**) and a cyclic C(BH)CH radical (**1**). In particular, for these two isomers, the calculated lengths for C—H, B—H, and B—C bonds are close to what is expected for the corresponding single bonds, while the C—C bond is close to an ethylenic one in the ring structure of the C(BH)CH radical and to an acetylenic one in the HBCCH structure. Finally, a band at 1995.2 cm^{-1} was associated with a C≡C motion coupled to B and H in an HBCC structure, where the two carbon atoms are not equivalent, while a strong band at 2039.3 cm^{-1} was linked to the C≡C stretching vibration of the HCCB radical. The thermochemistry of the possible reaction channels was also addressed by *ab initio* calculations.[14] Various pathways of boron atom approaches toward acetylene were considered: the addition of B atoms to the π bonds of acetylene toward one or both carbon atoms, leading either to the intermediate **i1** or **i2**, and the atomic boron insertion into one of the C—H acetylenic bonds, leading to the bent HBCCH intermediate (**i3**). All pathways were believed to be barrierless and strongly endoergic by about 280 kJ mol^{-1}. With the help of the matrix cage, the internal energy was proposed to stabilize **i2** to **2** and **i3** to **3**. Alternatively, intermediate **i2** could lose a hydrogen atom and undergo ring-opening to form the linear BCCH molecule **5**. In a similar way, intermediate **i3** could lose its excess energy via atomic hydrogen emission to yield the HBCC species **6**. Due to the instability of its structure, intermediate **i1** itself could not be isolated; however, its ring closure product (**1**) was detected. The latter could also lose a hydrogen atom, leading to a cyclic species (**4**). Alternatively, **i1** could isomerize, yielding **2** and/or **3**.[7] Recall, however, that, due to the nature of the matrix isolation studies, multiple pathways to the reaction products were proposed.

3.2.3. Reaction with Ethylene (C$_2$H$_4$)

In the matrix experiments on the reaction of laser-ablated boron atoms with ethylene (Figure 8), further small organo-
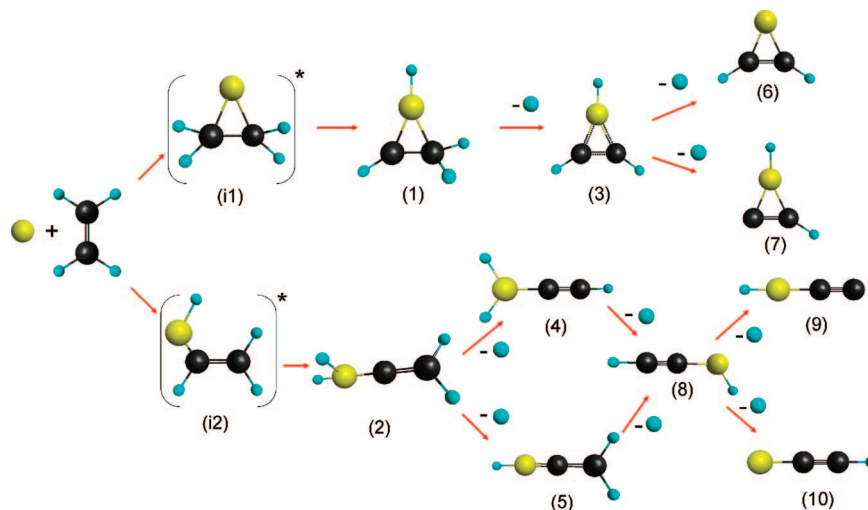
Figure 8. Proposed reaction mechanisms during the reaction of hyperthermal boron atoms with ethylene under matrix isolation conditions. Reprinted with permission from ref 16. Copyright 1998 American Chemical Society.

boron species have been identified via infrared spectroscopy using ^{10}B, ^{13}C, and D substitution combined with a comparison to BP86/6-311G* isotopic frequency calculations.[15,16,29,37] No bands were identified that could be assigned to the stabilized borirane radical intermediate CH$_2$(B)CH$_2$ (**i1**), even though this species is expected to be formed via boron atom addition to the ethylenic π bond.[16] This implies that the addition intermediate is not efficiently trapped and stabilized in the matrix. However, several bands could be associated with a cyclic isomer: the CH(BH)CH$_2$ molecule (**1**) that could be formed after a hydrogen migration from the CH$_2$ group to the boron atom in **i1**; this isomer is more stable than borirane (**i1**) by about 45 kJ mol^{-1} at the BP86 level of theory. The insertion of a boron atom into a C—H bond of ethylene should lead to the HBC$_2$H$_3$ radical (**i2**), which, however, could not be identified by any absorption bands. This also suggests that this species cannot be trapped under the matrix conditions. Several infrared bands (826.5, 847.7, 1347.1, 1770.6, 2568.7 cm^{-1}) were instead associated with the thermodynamically more stable H$_2$BCCH$_2$ structure (**2**)[16] possibly formed via hydrogen migration from the carbon to the boron atom. Additionally, three stable products of formula BC$_2$H$_3$ were observed and identified through DFT frequency calculations.[29,30] The small aromatic borirene molecule (**3**) formed by a hydrogen atom emission from **1** was characterized from five fundamental vibrational modes at 1175.3 cm^{-1} (associated with the symmetric B—C stretch), 1169.3 cm^{-1} (antisymmetric B—C stretch), 2639.6 cm^{-1} (B—H stretch), and 832.5/653.0 cm^{-1} associated with the out-of-plane hydrogen deformation. The aliphatic ethylborane H$_2$BCCH isomer (**4**) was identified via the B—H antisymmetric stretch at 2593.3 cm^{-1} and the C—C stretch at 2058.1 cm^{-1}, while the borallene isomer HBCCH$_2$ (**5**) was characterized via the B—H stretch at 2784.3 cm^{-1} and the B—C—C stretch at 1892.6 cm^{-1}. As for the reaction mechanism proposed,[15,16,29,30] the boron atom either can add to the π bond of ethylene, thus forming the cyclic (**i1**) intermediate or can insert into a C—H bond to yield the intermediate **i2**. The borirane radical (**i1**) is more stable than the reactant asymptote by about 160 kJ mol^{-1}, but it rearranges easily to the more stable isomer CH(BH)CH$_2$ (**1**), which is the major species observed in the matrix experiments.[16] CH(BH)CH$_2$ can lose a hydrogen atom and form the aromatic borirene (**3**). Due to the excess energy provided by laser ablation, the borirene molecule can further

lose a hydrogen atom and form CH(B)CH (**6**) and C(BH)CH (**7**) radicals, for which weak infrared bands were also observed. The vinylborane radical (**i2**) formed by insertion rearranges extensively to form the more stable allene-like species H$_2$BCCH$_2$ (**2**), which can lose an atomic hydrogen and form the closed shell species H$_2$BCCH (ethynylborane (**4**)) and HBCCH$_2$ (borallene (**5**)). Again, with their excess energy, both products can further lose one and/or two hydrogen atoms to form the bent HCCBH (**8**), the linear HBCC (**9**), and the linear BCCH (**10**) molecules.[16]

3.2.4. Reaction with Ethane (C$_2$H$_6$)

The last boron—hydrocarbon system studied under matrix conditions was the reaction of boron atoms with ethane (Figure 9).[16,38] Two stable products of general formula BC$_2$H$_5$ were observed. The stable vinylborane molecule (BH$_2$C$_2$H$_3$ (**1**)) has been identified through bands at 1536.8 cm^{-1} (C=C stretch) and 1031.3 cm^{-1} (out of phase CH$_2$ deformation) as well as isotopic counterparts of other bands around 2570.2 (BH$_2$ asymmetric stretch), 1414.1 cm^{-1} (CH$_2$ scissors), and 1213.9 cm^{-1} (BH$_2$ scissors).[16] Also, a methyl substituted compound CH$_3$B=CH$_2$ (**2**) was probed through a band at 1631.2 cm^{-1}, owing to the antisymmetric motion of the boron atom between the two carbon atoms. As for the reaction mechanism, similarly to the case of the reaction with methane, the reaction was proposed to proceed with the boron atom insertion into one of the carbon—hydrogen bonds of ethane, producing HBCH$_2$CH$_3$ (**i1**), which, in turn, isomerizes
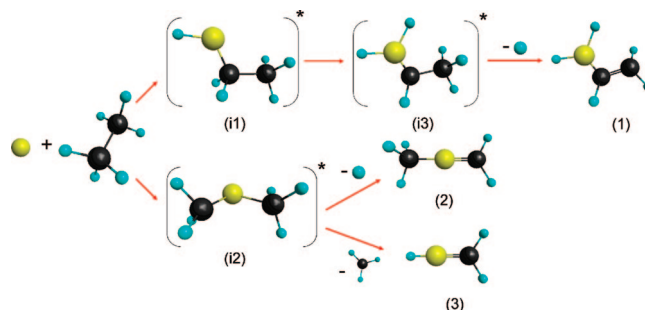

Figure 9. Proposed reaction mechanisms during the reaction of hyperthermal boron atoms with ethane under matrix isolation conditions. Reprinted with permission from ref 16. Copyright 1998 American Chemical Society.

Table 1. Products Observed via Infrared Spectroscopy in the Matrix Isolation Studies of the Reaction of Boron Atoms with Hydrocarbons

reactant	new products	reference
CH_4	CH_3BH	Jeong et al.[148]
CH_4	CH_3BH, H_2CBH_2, H_2CBH, $HCBH$, $HBCHBH$, $HBCBH$	Andrews et al.[11−13]
C_2H_2	$HBCCH$, cyclic-BC_2H_2, cyclic-HBC_2H, $HBCC$, $HCCB$, HBC_2	Andrews et al.[7,14]
C_2H_4	$(CH)_2BH$, CH_2BCCH, $HBCCH_2$, cyclic-$BHCHCH_2$, H_2BCCH_2, $HBCCH$, cyclic-BC_2H_2, cyclic-HBC_2H, $HBCC$, $HCCB$	Andrews et al.[15,16]
C_2H_6	$CH_3B{=}CH_2$, $H_2BC_2H_3$, $HBCH_2$ also all the products observed in the $B{-}C_2H_4$ reaction	Andrews et al.[16]

to BH_2CHCH_3 (**i3**) via hydrogen migration to boron. A subsequent hydrogen atom elimination from the terminal carbon gives the observed vinylborane (**1**). Differently from the case of methane, in the case of ethane, it is also possible that the boron atom inserts into a carbon−carbon bond, producing intermediate CH_3BCH_3 (**i2**). The latter, by losing

one of the hydrogen atoms, leads to the observed, stable $CH_3B{=}CH_2$ molecule (**2**). Also, CH_3BCH_3 can eliminate a methyl group to produce the observed species $CH_2{=}BH$ (**3**). Since the same products of the reaction with acetylene and ethylene were also observed, some extensive rearrangements including ring closure followed by molecular and atomic hydrogen loss are probably operative. Finally, the observation of boronhydride (BH), acetylene, and ethylene shows that another decomposition pathway for the initial insertion product is associated with the breaking of the newly formed B−C bond. In the same work[16] some preliminary results have also been reported on the reaction of boron with propane. In this case, no new organoborane species were identified and the most abundant products are the same as already seen for the boron plus ethylene reaction, that is, $CH(BH)CH_2$, BH_2CCH_2, borirene, ethylborane, and borallene. The speculated reaction mechanism implies that boron inserts into a carbon−hydrogen bond of propane, after which a methane elimination takes place, and the same intermediate species of the boron−ethylene reaction are formed. Two weak bands at 1697.0 and 1656.7 cm^{-1} were tentatively assigned to a $CH_2{=}BC_2H_5$ species.[16]
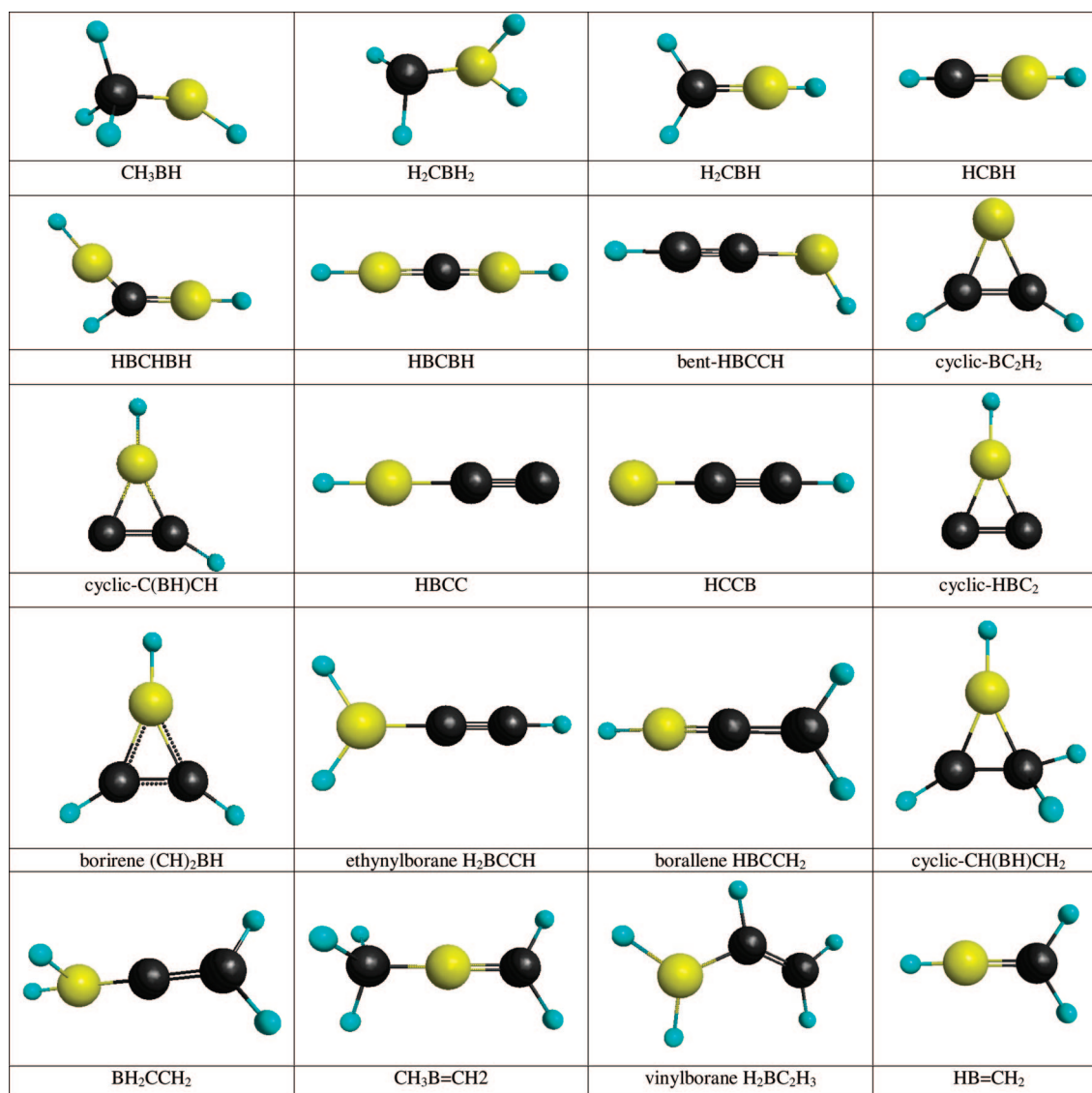
Figure 10. Compilation of the structures of novel organo-boron molecules formed during the reaction of boron atoms reacting with the hydrocarbon molecules methane, acetylene, ethylene, and ethane under matrix isolation conditions.

3.2.5. Reactions with Substituted Hydrocarbons

For completeness, although these reactants do not fall into the category of hydrocarbon molecules, we now summarize some studies on the reaction of laser-ablated boron atoms with substituted hydrocarbons.[22−25] In the case of the reactions with fluoro- (CH_3F), chloro- (CH_3Cl), and bromomethane (CH_3Br), two major products were identified via infrared spectra of isotopic combinations and density functional theory frequency calculations, that is CH_2BX and $CHBX$, where X = F, Cl, or Br.[25] In the case of the reactions with CH_3Cl and CH_3Br, also the primary insertion products (CH_3BCl and CH_3BBr), which were stabilized by the matrix, have been observed. The reaction mechanism suggested implies a boron atom insertion into the C−X bond followed by loss of one or two hydrogen atoms for all reactions.[25] In the reaction of boron atoms with methanol (CH_3OH), the principal detected product is CH_3BO.[24] The infrared spectra of various isotopic combinations and MP2 calculated isotopic frequencies also allowed identification of the minor products CH_2BOH and CH_2BO.[24] All new molecular species are formed via boron insertion into the C−O bond, while no products were formed via a boron atom insertion into a C−H bond. The HBO molecule was instead observed—possibly formed by insertion of boron into the O−H bond of methanol.[24] Finally, the reactions of laser-ablated boron atoms with methylamine and dimethylamine produce two iminoboranes (CH_3BNH and CH_3NBH) as well as the CH_2BNH_2 isomer, while CH_3BNCH_3 was also detected in the case of the reaction with dimethylamine.[23] For these systems, the observed products indicated that the primary reaction mechanisms involve boron insertion into either the C−N or N−H bonds.[23]

3.2.6. Summary of Matrix Isolation Studies

Pulsed laser evaporated boron atoms reacted with various hydrocarbons and carbon-containing substrates. A variety of novel organo-boron molecules, trapped in solid argon, have been identified via infrared analysis and with the help of *ab initio* quantum chemical calculations, which also derived the molecular structures of the new species. The species resulting from the reaction with hydrocarbon molecules are compiled in Table 1 and Figure 10. The generally good agreement between the theoretically predicted vibrational frequencies and the observed bands sustain the band assignments, especially if one takes into account that the calculated frequencies refer to "gas-phase" isolated molecules.

3.3. Dynamics Studies of Atomic Boron Reactions

3.3.1. Reaction with Acetylene (C_2H_2)

The differential cross sections for reaction of acetylene with ground state boron atoms were determined under single collision conditions by Balucani et al.,[5] Kaiser et al.,[223] and Zhang et al.[224] at collision energies of 12.9, 16.3, and 20.1 kJ mol^{−1}, respectively. The relative integral cross sections as a function of the collision energy were instead determined by Geppert et al.[6] in the range from 0.35 to 9.4 kJ mol^{−1}. Based on the collision-energy dependence of the differential cross section and on the comparison of the experimental data with high level electronic structure calculations, the authors suggested that the reaction is dominated by an atomic boron versus atomic hydrogen replacement mechanism leading to

the formation of two BC_2H isomers: the linear isomer $HBCC(X^1\Sigma^+)$ and the cyclic structure $c-BC_2H(X^2A')$, with the latter being about 4 kJ mol^{−1} more stable than the linear isomer (Figure 11a; Table 2). The combined experimental and theoretical investigations indicated that the ground state boron atom adds to the carbon−carbon triple bond of the acetylene molecule, yielding the cyclic intermediate **i1** (see Figure 11a). The **i1** intermediate undergoes two successive hydrogen atom migrations via **i2** to form the cyclic intermediate **i3**. Based on the shape of the derived center-of-mass translational energy distributions, we inferred that **i3** decomposes to the $c-BC_2H(X^2A')$ isomer plus atomic hydrogen via a tight exit transition state. The collision-energy dependence also indicated that **i3** isomerizes to **i4** prior to a hydrogen atom ejection, forming the linear structure, $HBCC(X^1\Sigma^+)$. Both the $c-BC_2H(X^2A')$ (**p1**) and HBCC $(X^1\Sigma^+)$ isomers (**p2**) are separated by an isomerization barrier to ring closure of only 3 kJ mol^{−1} with respect to HB-$CC(X^1\Sigma^+)$. Therefore, if $HBCC(X^1\Sigma^+)$ is formed with some internal excitation, it can rearrange to the $c-BC_2H(X^2A')$ structure and vice versa. Finally, the crossed beam studies confirmed the absence of a molecular hydrogen pathway and the formation of any BC_2 molecules. It is important to compare the gas phase dynamics studies with the mechanism derived from matrix isolation experiments (Figure 7). Here, in both investigations, the involvement of intermediates **i1**, **i3**, and **i4** was established;[7,14,223,224] also, the matrix isolation studies observed two isomers: the cyclic and the linear structures **p1** and **p2**, respectively.[7,14]

The crossed beam results by Balucani et al.,[5] Kaiser et al.,[223] and Zhang et al.[224] cannot be directly compared with those by Geppert et al.,[6] as in this last case only the excitation function was derived by detecting the hydrogen atom, which is formed in conjunction with **p1/p2**. Interestingly, the excitation function for the reaction of boron atoms with acetylene was seen to have a negative dependence; that is, the integral cross section decreases with the increase of the reactant collision energy. Nevertheless, the experimental trend shows a downward curvature at energies lower than 1 kJ mol^{−1}. The departure from linearity at low energy was interpreted as due to the presence of a small entrance barrier (∼0.18 kJ mol^{−1}) along the reaction path.

3.3.2. Reaction with Ethylene (C_2H_4)

Balucani et al.[212] and Zhang et al.[225] conducted the crossed beam study on the reaction of ground state boron atoms with ethylene at two collision energies of 17.6[212] and 20.1 kJ mol^{−1},[225] respectively (Figure 11b; Table 2). In this case as well, the experimental results were complemented by electronic structure ab initio calculations.[212,225] Under single collision conditions, the reaction was found to be barrierless and dictated by an addition of the boron atom to the carbon−carbon double bond to either one or both carbon atoms, yielding intermediates **i2** and **i1**, respectively (see Figure 11b). Intermediate **i2** was found to be very unstable and easily rearranges via ring closure through a barrier of only 1 kJ mol^{−1} to **i1**, which in turn isomerizes to a second, more stable cyclic intermediate **i3**. According to the characteristic of the differential cross sections, it was concluded that this structure decomposes via a tight exit transition state to form the heteroaromatic borirene molecule, $BC_2H_3(X^1A_1)$ (**p1**), plus atomic hydrogen.[212,225] Statistical RRKM calculations predicted that the most important reaction channel is an alternative pathway: the isomerization of **i3** via ring-
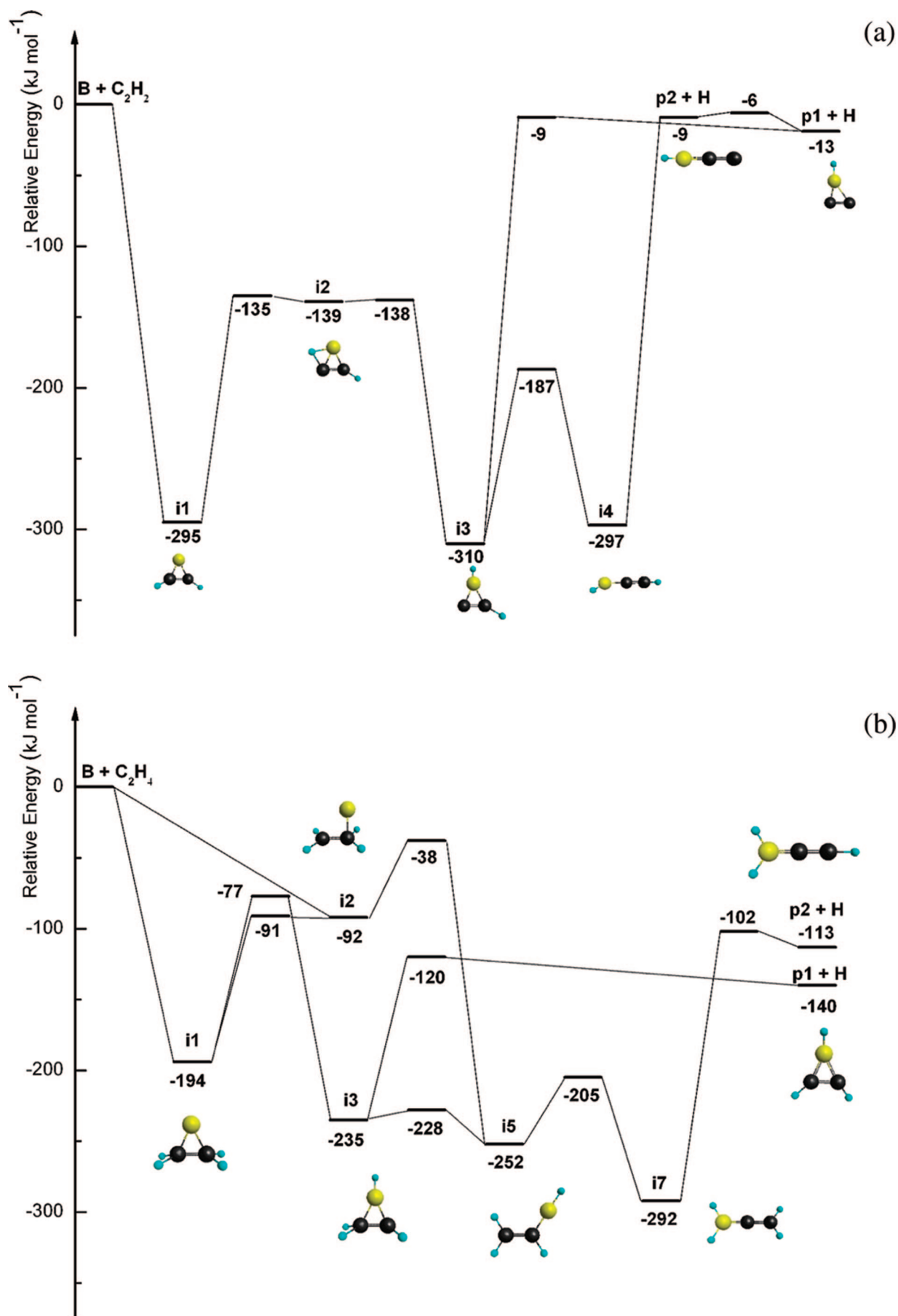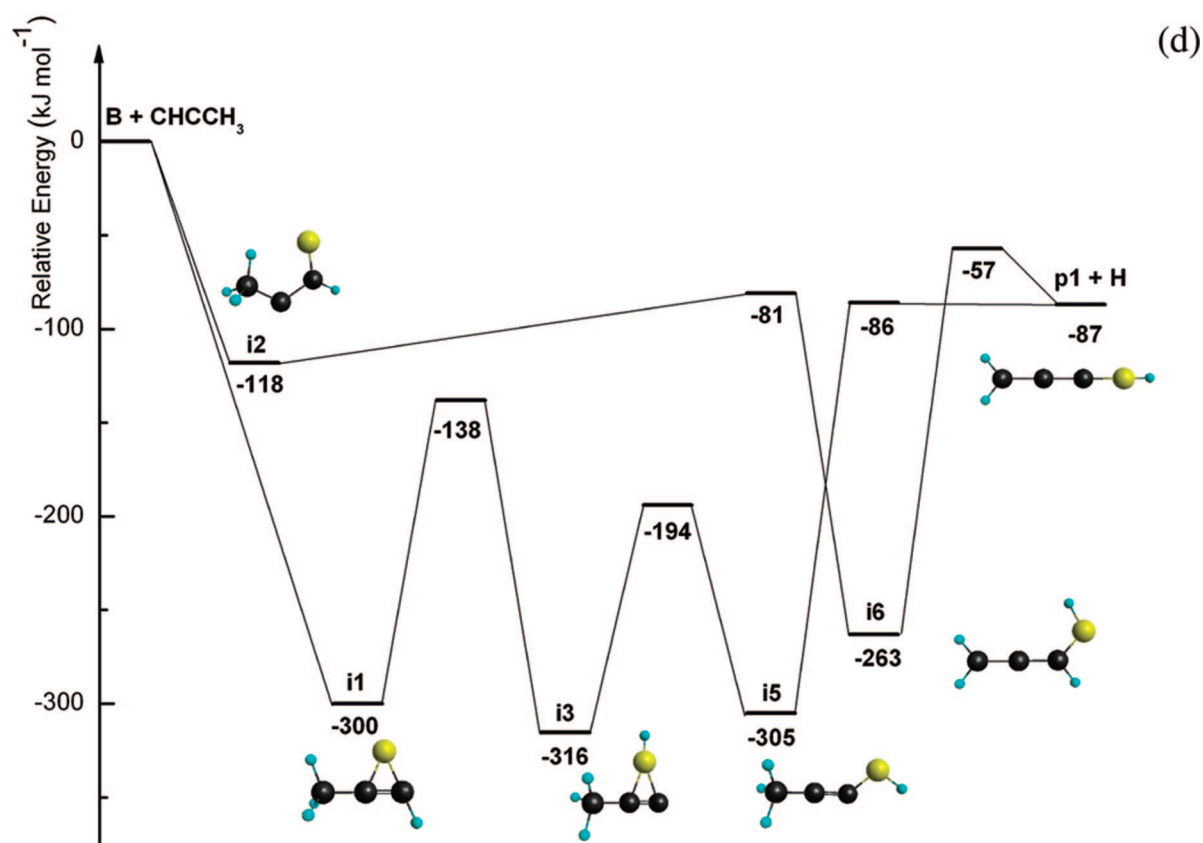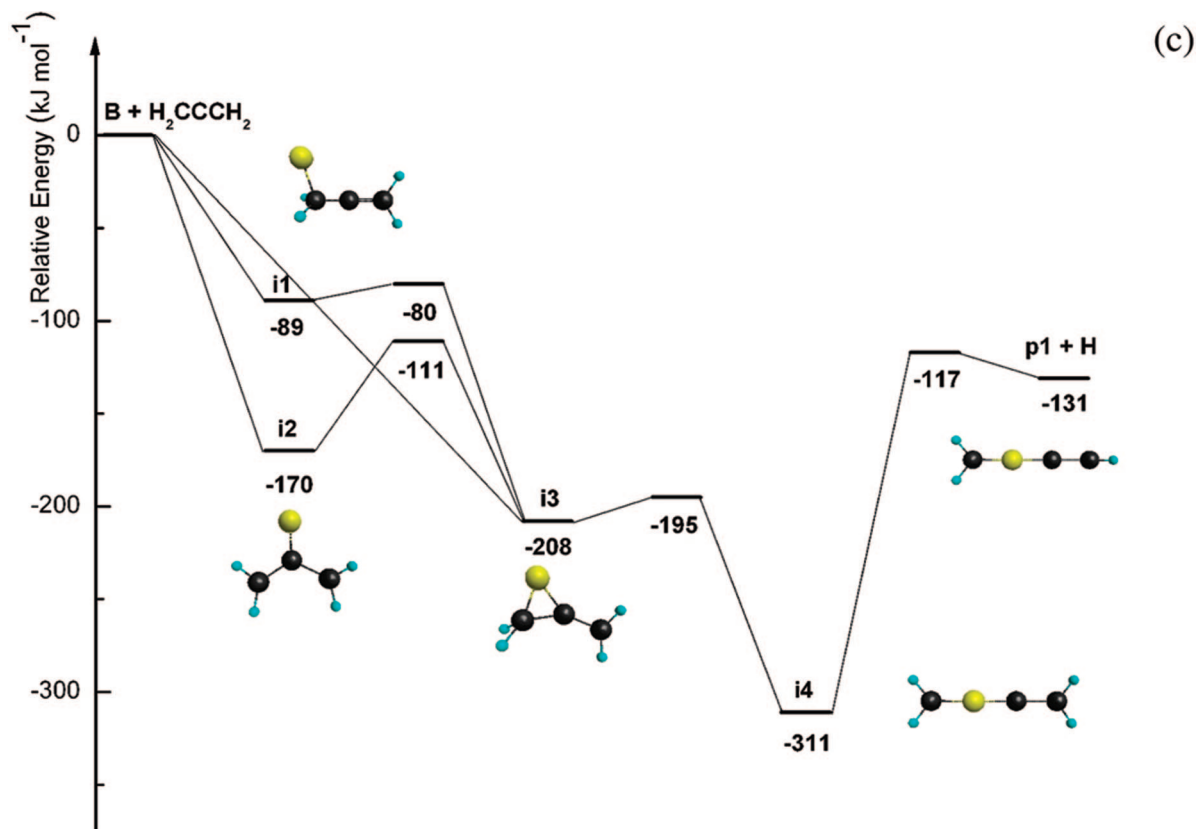
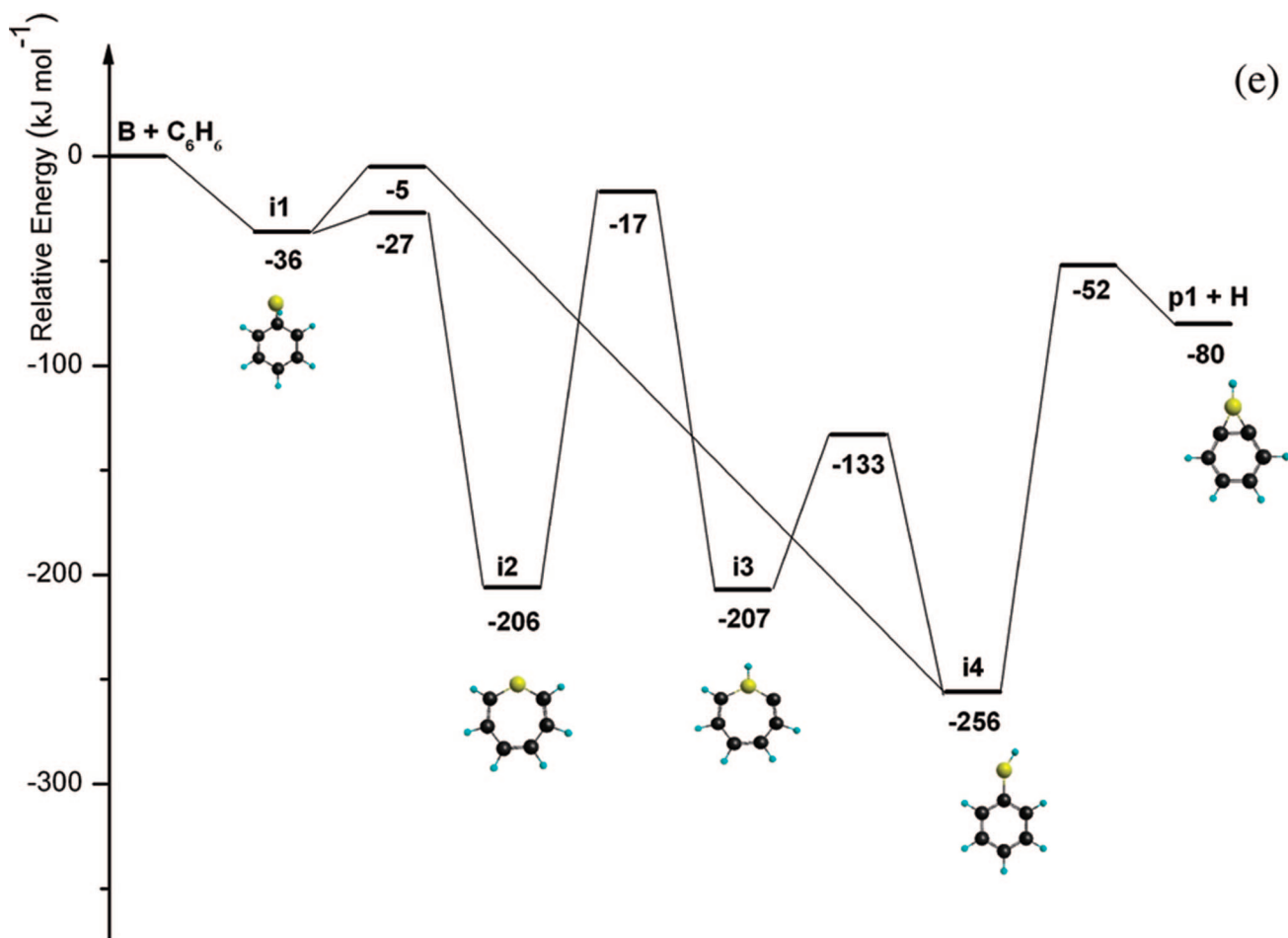**Figure 11.**

(c)

(d)

(e)

Figure 11.

Figure 11. Sections of potential energy surfaces (PESs) relevant to the formation of organo molecules in the bimolecular gas phase reactions of ground state boron atoms with the hydrocarbon molecules (a) acetylene [Reprinted with permission from ref 224. Copyright 2007 Elsevier]; (b) ethylene [Reprinted with permission from ref 225. Copyright 2008 American Chemical Society]; (c) allene [Reprinted with permission from ref 226. Copyright 2007 American Chemical Society]; (d) methylacetylene [Reprinted with permission from ref 227. Copyright 2008 Wiley—VCH]; and benzene (e) [Reprinted with permission from ref 228. Copyright 2007 Elsevier].

opening to **i5** followed by a hydrogen shift to **i7**. The latter fragmented to the thermodynamically less stable isomer **p2** ($BC_2H_3(X^1A_1)$) plus hydrogen.[225] Nevertheless, the results of the dynamic studies suggest that statistical treatment of the atomic boron—ethylene reaction is not warranted for this system. In a similar manner as found in the boron—acetylene system, multiple reaction intermediates (**i1**, **i3**, **i5**, **i7**) and the products **p1** and **p2** were identified also in the matrix experiment (Figure 8). This demonstrates the complementary character of the crossed beams and matrix studies to isolate the intermediates and to detect them via infrared spectroscopy on one hand in the matrix and to infer them from the center-of-mass functions.
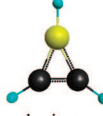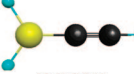
3.3.3. Reaction with Allene (H₂CCCH₂)
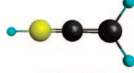
Only a single study of the reaction of boron with allene under single collision conditions exists at a collision energy of 21.5 kJ mol^{-1} (Figure 11c; Table 2).[226] The reaction dynamics were found to be indirect and initiated by an addition of the boron atom to the π-electron density of the allene molecule; three entrance channels were identified in which the boron atom adds to the terminal carbon atom, to the central carbon atom, or to two carbon atoms simultaneously, yielding the reaction intermediates **i1**, **i2**, and **i3**. Both **i1** and **i2** can rearrange to yield ultimately **i3**. The latter, which is stabilized by 208 kJ mol^{-1} with respect to the
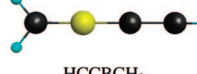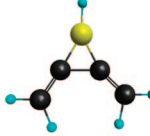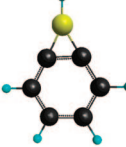
separated reactants, undergoes ring-opening to an acyclic intermediate H_2CCBCH_2 (**i4**). This structure was found to be the global minimum and long-lived with respect to its rotational period and decomposed via an atomic hydrogen loss through a tight exit transition state located about 14 kJ mol^{-1} above the separated products to the closed shell, C_{2v} symmetric molecule $HCCBCH_2$ (**p1**).[226]

3.3.4. Reaction with Methylacetylene (CH₃CCH)

The gas phase reaction of atomic boron with methylacetylene was investigated at a collision energy of 21.6 kJ mol^{-1} to untangle if a distinct isomer—here allene and methylacetylene—can form different product isomers.[227] Since the hydrogen atoms in methylacetylene are not equivalent, studies were also conducted with D3- and D1-methylacetylene to determine experimentally to what extent the hydrogen atom is emitted from the methyl and/or acetylenic group. Based on the isotopic substitution studies, the following dynamics emerged (Figure 11d; Table 2). The results suggested that the reaction follows indirect scattering dynamics and proceeds at least through two reaction channels. The boron atom can add to the carbon—carbon triple bond of the methylacetylene molecule, forming two initial collision complexes. These are **i1** via addition to both carbon atoms and **i2** through an addition of the boron atom to the terminal carbon atom (α carbon). The latter pathway is directed by

Table 2. Compilation of Crossed Beams Studies of Reactions of Boron Atom with Hydrocarbons

reactant	collision energy, kJ mol⁻¹	products	reference
C_2H_2	12.9/16.3	linear-HBCC	Kaiser et al.[5,223]
C_2H_2	0.35 - 9.4	not identified	Geppert et al.[6]
C_2H_2	20.1	linear-HBCC, Cyclic-BC₂H	Zhang et al.[224]
C_2H_4	17.6	borirene	Balucani et al.[212]
C_2H_4	20.1	borirene, H₂BCCH, H₂CCBH	Zhang et al.[225]
CH_3CCH	21.6	H₂CCCBH	Zhang et al.[227]
H_2CCCH_2	21.5	HCCBCH₂	Zhang et al.[226]
CH_3CCCH_3	17.9	1,2-dimethyene-3-bora-cyclopropane	Sillars et al.[231]
D6-benzene	23.1	D5-benzoborirene	Kaiser et al.[229,230]
benzene	24.5	benzoborirene	Zhang et al.[230]

the steric effect of the CH_3-group and the enhanced cone of acceptance of the α carbon atom compared to the β carbon atom (the carbon atom to which the methyl group is connected). Intermediate **i2** was found to isomerize via hydrogen shift from the methyl group to the boron atom, yielding **i6**, which then decomposed to the C_{2v} symmetric H₂CCCBH isomer (**p1**) plus atomic hydrogen. On the other hand, intermediate **i1** was long-lived and underwent multiple isomerizations involving hydrogen shifts to **i3** and ring-opening to **i5**. The latter also underwent hydrogen emission to form **p1**. Utilizing the CD₃CCH reactant, both channels lead ultimately to the formation of two isotopomers, i.e. the C_{2v} symmetric D₂CCCBH and D₂CCCBD structures. The atomic deuterium replacement channel could be explained in terms of the statistical, unimolecular decomposition of a reaction intermediate **i5** and the involvement of the reaction sequence **i1** → **i3** → **i5** → **p1** + D, whereas the atomic hydrogen loss pathway can only be accounted for with a

non-RRKM behavior of the system through intermediate **i6**. This reaction presents the second case besides the boron−ethylene reaction, which does not follow a statistical pattern. Second, the crossed beam experiments provided explicit evidence that the reaction of boron with allene and methylacetylene yielded two distinct isomers, i.e. the C_{2v} symmetric closed shell H₂CBCCH and H₂CCCBH molecules.[227]

3.3.5. Reaction with Benzene (C₆H₆)

The reaction of ground state boron atoms with benzene[228] and D6-benzene[228−230] was explored in crossed beam experiments at collision energies of 24.5[228] and 23.1 kJ mol⁻¹,[229,230] respectively, to study the reactivity of aromatic molecules (Figure 11e; Table 2). Here, the first step in finding the actual reaction mechanism is to identify the reaction product(s). For this, the experimentally determined reaction energy was compared with the computational data, and it was established that the aromatic benzoborirene isomer BC₆H₅ (**p1**) plus atomic hydrogen is an open channel. In strong contrast to the previous systems, in the case of the boron−D6-benzene reaction, the ¹¹BC₆D₆ adduct was clearly identified.[229] This finding indicates that the reactions of atomic boron with benzene and D6-benzene are indirect and proceed through a long-lived intermediate via a boron addition−hydrogen/deuterium atom elimination pathway. As expected for reactions of electron deficient boron atoms with unsaturated hydrocarbons, the intermediate **i1** results from the B addition to the benzene ring. The isomerization of **i1** ultimately lead to the phenylboryl radical **i4** via ring-opening of **i1** to **i2** and hydrogen shift to **i3**; these steps do not involve barriers higher than the energy of the separated reactants. Phenylboranyl was found to decompose via cleavage of an ortho-carbon−hydrogn bond and concomitant ring-closure to yield ultimately the benzoborirene product via a tight exit transition state located about 29 kJ mol⁻¹ above the products. The center-of-mass angular distributions verify the computed geometry of the exit transition state. The distributions peaked at 90°, which is indicative of a reversed addition of a hydrogen/deuterium atom perpendicular to the molecular plane of the ¹¹BC₆H₅/¹¹BC₆D₅ benzoborirene molecules. Here, the hydrogen/deuterium atom adds to the π-electron density of the aromatic benzoborirene species at the bridge-carbon atom perpendicularly to the molecular plane. This approach geometry leads to the largest orbital overlap and, hence, presents the lowest energy pathway via addition.

3.3.6. Reaction with Dimethylacetylene (CH₃CCCH₃)

Finally, the bimolecular reaction of boron atoms with dimethylacetylene was investigated at a collision energy of 17.9 kJ mol⁻¹;[231] this study was aimed to rationalize the effect of a hydrogen atom replacement of the acetylenic group in methylacetylene by a methyl group on the reaction dyamics. The experimental results depicted that, once again, the bimolecular collision between a boron atom and an unsaturated hydrocarbon leads to a heavy reaction product via a B/H exchange pathway leading to the formation of a BC₄H₅ isomer. A comparison of the experimentally derived reaction energy with those derived computationally indicates the formation of the 1,2-dimethyene-3-boracyclopropane isomer (Table 2). Here, ground state boron was suggested to attack the carbon−carbon triple bond of the dimethylacetylene molecule at two carbon atoms to form a cyclic BC₄H₆ intermediate; the latter was proposed to undergo hydrogen

transfer from the methyl group to the boron atom. This complex then fragments to atomic hydrogen plus a cyclic 1,2-dimethylene-3-bora-cyclopropane molecule via a tight transition state.

4. Summary

This review article compiles recent studies on the reactivity of boron atoms with organic molecules—predominantly hydrocarbons—leading to the formation of novel organo-boron species, with the characterization of their formation mechanisms. The studies summarized here comprise kinetic and matrix isolation experiments, crossed molecular beam studies, and theoretical investigations of the underlying potential energy surfaces. The gas phase kinetics studies of atomic boron reactions provided unique information on the reaction rate. These data can be provided neither by matrix isolation studies nor by crossed beam experiments. Nevertheless, since in the kinetics investigations the rate constants were derived by observing the decay of the concentration of the boron atom reactant, kinetics studies cannot deliver important information on the reaction products, the intermediates involved, and, hence, the reaction mechanisms. On the one hand, the matrix isolation experiments have the unprecedented capability to observe the reaction intermediates—if they can be stabilized in the matrix—and sometimes the reaction products spectroscopically, predominantly via infrared spectroscopy. Since these studies were not conducted under single collision conditions, it is difficult, however, to untangle the underlying reaction mechanisms and extract information on the chemical dynamics. Likewise, since the boron atoms are generated via laser ablation, it is unknown to what extent the atoms are generated in their electronic ground or excited state. This is crucial, since the reactivity strongly depends on the electronic state. Finally, cage effects from the matrix can influence the outcome of the reaction, and the main reaction products and intermediates might be different from those observed under single collision conditions in the gas phase. On the other hand, the third experimental approach illustrated—the crossed beam technique—has the advantage that both reactants can be prepared under well-defined experimental conditions in separate supersonic beams. Because of the large mean free path, achieved by operating at a very low pressure, the products are formed only at the collision center and then fly undisturbed toward the detector. This eliminates completely the possible wall effects of bulk experiments and the cage effect of matrix experiments. Further, the spin state of the reacting boron atoms can be controlled. Based on the mass-to-charge ratio of the observed product(s) and the energetics, the product isomer can be identified unambiguously. Mechanistical studies can be further expanded by utilizing (partially) deuterated reactants in those cases in which the hydrogen atom(s) of the secondary reactant are not chemically equivalent.

In conclusion, the chemistry that controls the formation of organo-boron compounds in combustion chemistry, astrochemistry, weakly ionized plasmas, material sciences, and CVD processes has partially been unveiled. A more general conclusion is that, due to the advantages but also limitations of each of the experimental approaches presented here, only a combined effort including kinetics and matrix isolation experiments as well as crossed molecular beam and theoretical studies can allow us to understand the chemical reactivity of systems of increasing complexity, such as those described in this review.

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