

MAY 2017

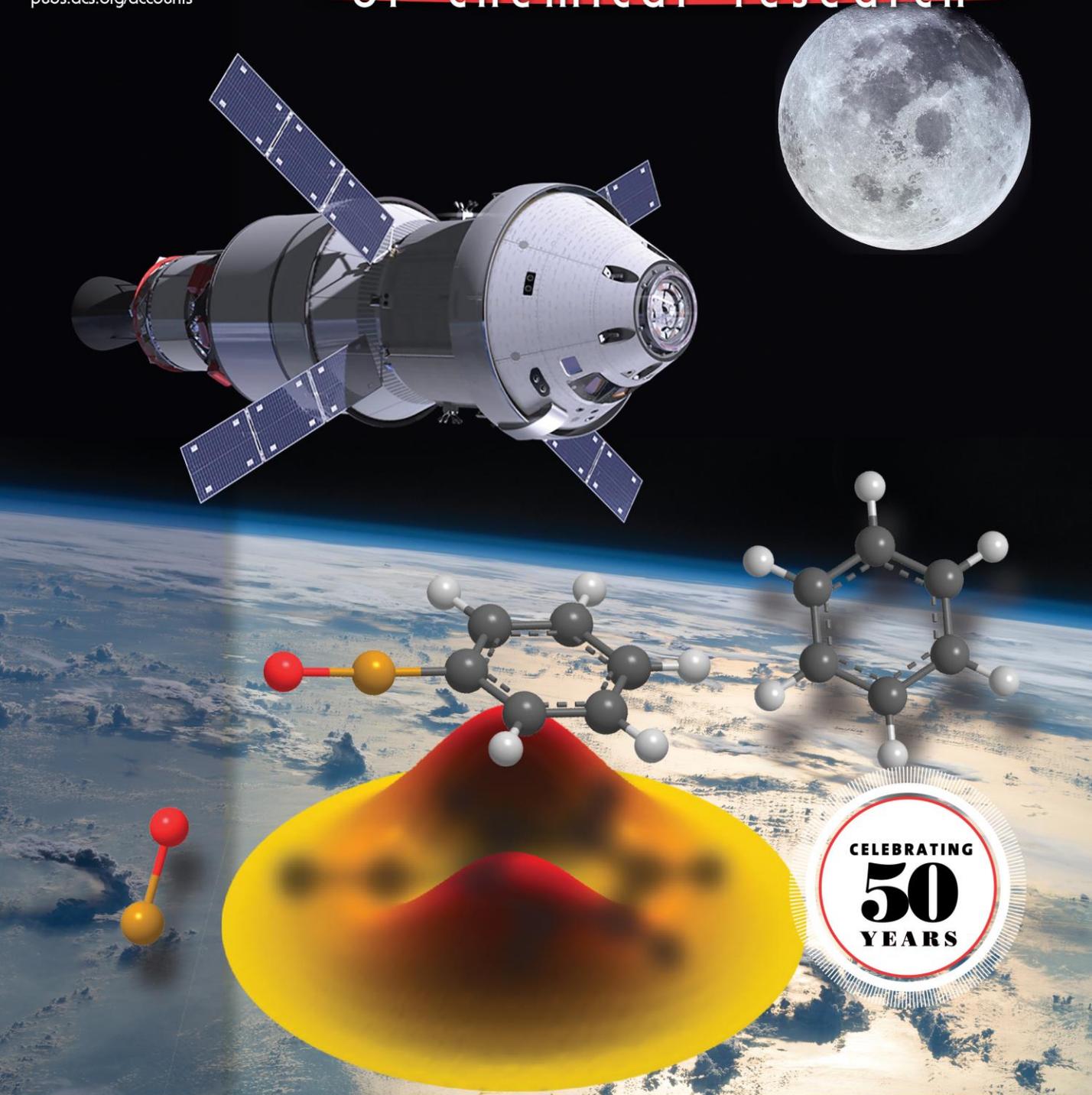
VOLUME 50

NUMBER 5

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Exploring the Gas Phase Synthesis of the Elusive Class of Boronyls and the Mechanism of Boronyl Radical Reactions under Single Collision Conditions

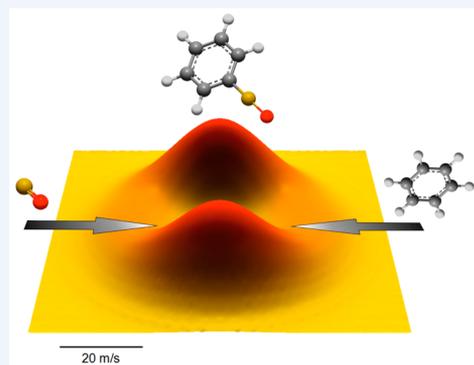
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CONSPECTUS: Until recently, the chemistry of boronyl (BO), a diatomic radical isoelectronic with the cyano (CN) species, has remained unknown. The boronyl group is characterized by a boron–oxygen multiple bond, and because of the inherent electron deficiency of the boron atom, boronyls (RBO) are highly reactive and typically only exist in their cyclotrimeric form (RBO)₃. Due to their invaluable role as reactants, the isolation of the monomers in gas phase experiments has been extensively sought after by the organic synthesis and physical organic chemistry communities but never achieved. Besides the interests from a physical organic and synthetic point of view, boronyls also play a role as reaction intermediates in boron-assisted rocket propulsion systems. In this Account, we review recent experimental work in which gas phase organo boronyl monomers (RBO) are formed via bimolecular reactions of the boronyl radical (BO) with C2–C6 unsaturated hydrocarbons. The investigated hydrocarbons are widely exploited as fuels, and their reactions with boronyl radicals under single collision conditions lead to the formation of organo boronyls. Our studies also elucidate the mechanisms of their formation reactions thus furnishing a comprehension at the molecular level of this reaction class. The variety of the employed hydrocarbon substrates has allowed us to systematically classify the chemical behavior of the boronyl radicals. With the exception of the case of the dimethylacetylene reaction, the boron monoxide radical versus atomic hydrogen exchange mechanisms were always open leading to the formation of highly unsaturated organo boronyl monomers (RBO), which could be easily identified because they cannot trimerize under single collision conditions.

Besides the hydrogen displacement pathway, methylacetylene, dimethylacetylene, and propylene, carrying one or two methyl groups, were also found to eliminate a methyl group. In all systems, the reactions were barrierless, indirect, and initiated by addition of the boron monoxide radical to the π electron density of the hydrocarbon molecule, with the radical center located at the boron atom of the BO radical, thus leading to doublet radical intermediates. These intermediates either decompose via hydrogen or methyl loss or isomerize prior to their decomposition via atomic hydrogen or migration of the BO moiety. A consistent trend suggests that all exit transition states are rather tight with those involved in the hydrogen atom loss depicting exit barriers of typically 25 to 35 kJ mol⁻¹, whereas the methyl loss pathways are associated with tighter exit transition states located about 30–50 kJ mol⁻¹ above the separated products. Further, the overall energetics suggest that those bimolecular reactions are exoergic by 40–90 kJ mol⁻¹. These findings confirm that this reaction class leads to the formation of highly unsaturated organo boronyl molecules.



I. INTRODUCTION

Until recently, the boronyl (BO) chemistry has remained largely elusive, although the BO moiety is isoelectronic to the cyano group (CN) and both the boronyl and the cyano radicals represent monovalent σ radicals holding $^2\Sigma^+$ electronic ground states. Their isoelectronicity is also well reflected in similar bond energies (799 kJ mol⁻¹ versus 749 kJ mol⁻¹), ionization energies (13.3 eV versus 13.6 eV), and bond lengths of 1.205 Å versus 1.172 Å, respectively.¹ Nevertheless, whereas the cyano group can be well represented by a carbon–nitrogen triple bond, the boronyl group has been mainly characterized as a boron–oxygen double bond. Considering mesomeric resonance structures, however, the boron–oxygen bond could have also a triple bond character.^{2–4} A recent work supports, indeed, that in

coordination spheres of late transition metals, the boron–oxygen bond is better represented by a triple bond.⁵ The inherent electron deficiency of the boron atom, which classified boron as a Lewis acid, is also responsible for the enhanced reactivity of boronyls (RBO) compared to the relatively inert nitriles (RCN) with “R” being an organic side group with Lewis bases. Therefore, organic boronyls, or organyl oxoboranes, exist in their cyclotrimeric forms, (RBO)₃, rather than as monomers.⁶ Consequently, the isolation of the corresponding monomers in the gas phase rather than via matrix isolation experiments⁷ has not been achieved, even if it has been pursued by many research

Received: March 31, 2016

Published: December 19, 2016



groups because of their invaluable role as reactants in reactions like Suzuki cross-coupling reactions and as ligands in platinum coordination centers, where recent advances synthesized complexes immune to oligomerizations.⁸

Besides the interests from the physical organic and synthetic organic chemistry communities, boronyls have been also implicated as reaction intermediates in boron-assisted rocket propulsion systems, mainly with involvements in air-breathing, ramjet, and scramjet systems, where high energy content per mole and high energy content per volume and molecular weight are necessary.^{9–11} The energy density of boron (59.0 kJ g^{-1}) is significantly higher than those of conventional liquid hydrocarbon fuels like gasoline and diesel of typically 46 kJ g^{-1} and is greater than that of aluminum (31.0 kJ g^{-1}) or magnesium (24.0 kJ g^{-1}), which are considered the most popular metal additives. The complete conversion of boron to boron oxide (B_2O_3) via the reaction with oxygen releases up to 630 kJ mol^{-1} , which is three times larger than the energy released by the best hydrocarbon jet propellants (JP-10). Nevertheless, the formation of B_2O_3 , an inert layer that coats the nonreacted boron, prevents further reaction, and the oxidation of boron does not reach full energy release.¹² For this reason, the oxidation of boron is very different with respect to that of hydrocarbons, where gaseous carbon dioxide (CO_2) is formed. Indeed, boron combustion occurs in two steps:^{13,14} (1) in the first step, the ignition stage, a weak glowing removes the oxide layer via gasification; (2) in the second step, the real combustion phase, a vigorous burning, of a heterogeneous type due to the high boiling point of boron ($3900\text{--}4140 \text{ K}$), occurs.

Nowadays, boron can be used in the form of pellets together with conventional carbon-based fuels. The carbon-based fuel ignites and reaches a high enough temperature to remove the boron oxide layer, which, in turn, allows clean boron to be accessible for the combustion phase. To simulate the core parts of the combustion cycle and, in particular, the diffusion rates through the boron oxide layers of oxygen and boron, numerous models have been proposed and reported in the literature. By relying on the experimental work by Macek et al.,^{15,16} King first developed a model¹³ where the diffusion rate of oxygen through the oxide layer is the rate-determining step. This approach was later confuted by Ulas et al.⁹ who, in contrast, suggested a model where it was the diffusion of boron through the oxide layer that was the rate-determining step⁹ (as of today, the question of which of the two diffusion processes is dominant has remained unanswered). The approach used in the Ulas et al.'s model makes use of generic global reactions in three stages: particle heating without reaction (ignition delay), first stage of combustion (oxide layer removal), and second stage of combustion (clean boron oxidation). In 1999, Zhou et al.¹⁴ developed a gas-phase kinetic model for the homogeneous chemistry of a B/O/H/C/F combustion system, but the absence of reliable experimental data was recognized by the authors as limiting the accuracy of their work. Information on the rate coefficients of many supposedly important reactions and their product branching ratio is lacking. Nevertheless, the model by Zhou et al.¹⁴ remains the most comprehensive available in the literature, and it is used as a reference for simpler models like those of Hussmann and Pfitzner^{17,18} Overall, the boron/carbon fuel approach is energetically costly, and a refinement of the process is required. This in turn requires detailed knowledge of the organo boronyls formed in the combustion processes.

In this Account, we review recent experimental work in which gas phase organo boronyl monomers (RBO) are formed via

bimolecular reactions of the boronyl radical (BO) with C2–C6 unsaturated hydrocarbons. These hydrocarbons are widely exploited as hydrocarbon fuel, and their reactions with boronyl radicals under single collision conditions access the hitherto largely elusive class of organoboronyls; these investigations also explore the reaction dynamics and mechanisms of their formation thus providing versatile reaction pathways to synthesize chemically more complex organo boronyl in prospective laboratory investigations of this reaction class.

II. EXPERIMENTAL APPROACH

The most versatile experimental technique to investigate bimolecular reactions at the molecular level is the crossed molecular beam (CMB) method combined with mass spectrometric (MS) detection.^{19,20} Differently from flow kinetics experiments, the CMB approach permits investigating reactive collisions without any interference of secondary or wall collisions. The reactants are not simply combined together but are rather produced into two distinct separate beams, which are made to collide at a specific collision energy and crossing angle. The products are generated only in the collision region, from which they fly toward the detector without any interference because of the large mean free path achieved by operating at very low pressures in the ultrahigh vacuum region. In this way, it is possible to achieve scattering observables of well-defined molecular encounters. On the other hand, the mass spectrometric detection makes this experimental approach universal, as any molecular product can be detected. This is particularly important when the reaction products are uncharacterized molecular radicals, the spectroscopic properties of which are totally unknown. In its original development, mass spectrometric detection is preceded by high energy electron (hard) impact ionization, while in its most evolved versions, mass spectrometric detection is accompanied by ionization achieved with tunable VUV synchrotron radiation²¹ or soft electron impact ionization.²²

Briefly, the apparatus employed to obtain the results presented here consists of two source chambers posed at 90° , a large stainless steel scattering chamber, and a ultrahigh-vacuum quadrupole mass spectrometric (QMS) detector (maintained at pressures lower than 10^{-11} Torr), which can be rotated in the collision plane with respect to the collision center. In the primary source, a pulsed supersonic boronyl $\text{BO}(X^2\Sigma^+)$ radical beam is generated in situ by laser ablation of a solid boron rod and reaction of the ablated boron atoms with carbon dioxide, which also acts as a seeding gas.²³ Laser ablation of boron was achieved by focusing the output of the fourth harmonic (266 nm) of a Spectra-Physics Quanta-Ray Pro 270 Nd:YAG laser (3–10 mJ) operating at 30 Hz onto a boron rod performing helical motion. The boron rod (80% ^{11}B , 20% ^{10}B) was mounted on a homemade ablation source^{24,25} placed in the primary source region of the vacuum chamber. The molecular beam containing the boronyl radical passes through a skimmer into the main chamber of the machine. The supersonic expansion cools down the internal states of BO and only the ground vibrational level and lowest rotational levels are populated, as verified by a laser-induced fluorescence characterization of the beam.²³ A four-slot chopper wheel selects a slice of boron monoxide with a well-defined velocity distribution. At the interaction region, the boronyl radical collides with the second pulsed beam of the unsaturated hydrocarbon at typical collision energies in the $10\text{--}40 \text{ kJ mol}^{-1}$ range. The scattered products are detected by a quadrupole mass spectrometer preceded by an electron impact ionizer as a function of the scattering angle. Time-of-flight

(TOF) distributions are so recorded at the mass-to-charge ratios (m/z) of interest. To interpret the raw data and infer the reaction mechanism, it is necessary to transform the laboratory data into the center-of-mass (CM) system using a forward-convolution routine. In this procedure, trial angular, $T(\theta)$, and translational energy, $P(E_T)$, distributions in the CM reference frame are used to simulate the laboratory data, taking into account the transformation Jacobian and the averaging over the apparatus and beam functions. The procedure is repeated until the best-fit of the scattering data is achieved. Best-fit $T(\theta)$ and $P(E_T)$ are used to generate the product flux contour map (differential cross section), where the intensity of the products is reported as a function of the CM scattering angle, θ , and product velocity, u . The contour map is a snapshot of the reactive collision and contains all the relevant information on the reaction mechanism.

III. RESULTS AND DISCUSSION

In this section, we report our experimental results on the reactions of the boronyl radical with multiple C2–C6 unsaturated hydrocarbons. To present the results, we have grouped these

systems based on the functional groups of the involved hydrocarbons: (1) acetylenes carrying a carbon–carbon triple bond [acetylene ($\text{H}-\text{C}\equiv\text{C}-\text{H}$),²⁶ methylacetylene ($\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$),²⁷ and dimethylacetylene ($\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$)²⁸] to systematically explore the effect of the hydrogen atom substitution by one or two methyl groups (Table 1, Figure 1); (2) olefins holding a carbon–carbon double bond [ethylene ($\text{H}_2\text{C}=\text{CH}_2$)²⁹ and propene ($\text{CH}_3-\text{CH}=\text{CH}_2$)³⁰] (Table 2, Figure 2), and (3) highly unsaturated hydrocarbons with multiple double or triple bonds [allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$),³¹ diacetylene ($\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$),³² 1,3 butadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$),³³ and benzene (C_6H_6)³⁴] (Table 3, Figure 3). The reaction with allene when compared to the reaction with its isomer methylacetylene or the reaction with dimethylacetylene when compared to the reaction with its 1,3-butadiene isomer reveal effects associated with the stereospecificity of the boronyl radical attack. Notably the reaction with benzene is the prototype for the series of reactions of boronyl radicals with aromatic hydrocarbons. In all cases, the CMB results have been interpreted in the light of electronic structure calculations performed

Table 1. Summary of Key Results of the Crossed Beam Reactions of the Boron Monoxide Radical with Acetylene, Methylacetylene, And Dimethylacetylene

hydrocarbon reactant	collision energy, kJ mol^{-1}	experimental (theoretical) reaction energy, kJ mol^{-1}	experimental (RRKM) branching ratio, %
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	13.0 ± 0.8	$\text{H}-\text{C}\equiv\text{C}-\text{BO} + \text{H}$ [1] -62 ± 8 (-58 ± 10) ^a	100 (100)
$\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$	22.7 ± 1.2	$\text{C}_3\text{H}_3\text{BO} + \text{H}$ -82 ± 16	
		$\text{CH}_3\text{CCBO} + \text{H}$ [2] (-82 ± 10) ^b	40 ± 5 (38)
		$\text{CH}_2\text{CCHBO} + \text{H}$ [3] (-43 ± 10) ^b	4 ± 3 (1)
		$\text{HCCBO} + \text{CH}_3$ [1] (-78 ± 23) ^b (-85 ± 10) ^b	56 ± 15 (61)
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$	23.9 ± 1.5	$\text{CH}_3\text{CCBO} + \text{CH}_3$ [2] -91 ± 22 (-105 ± 10) ^c	100 (99)

^aCCSD(T)/cc-pVTZ.²⁶ ^bCCSD(T)/CBS.²⁷ ^cCCSD(T)/cc-pVTZ.²⁸

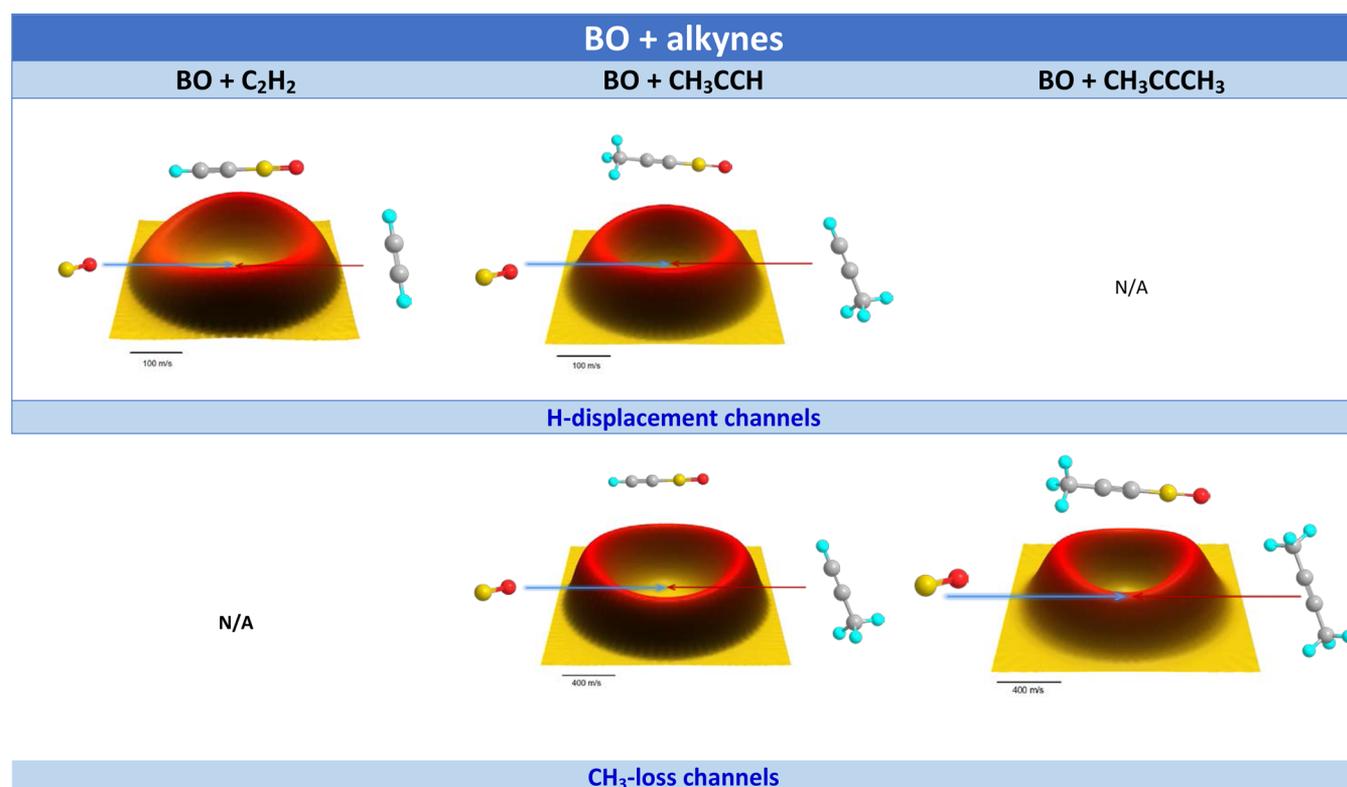


Figure 1. Flux contour map of the reactions of the boronyl radical with acetylene (H-loss), methylacetylene (H- and CH_3 -loss), and dimethylacetylene (CH_3 -loss).

Table 2. Summary of Key Results of the Crossed Beam Reactions of the Boron Monoxide Radical with Ethylene and Propylene

hydrocarbon reactant	collision energy, kJ mol^{-1}	experimental (theoretical) reaction energy, kJ mol^{-1}	experimental (RRKM) branching ratio, %
$\text{H}_2\text{C}=\text{CH}_2$	12.2 ± 0.6	$\text{C}_2\text{H}_3\text{BO} + \text{H}$ [4] -42 ± 11 (-39 ± 10) ^a	100 (100)
$\text{CH}_3\text{CH}=\text{CH}_2$	22.5 ± 1.3	$\text{C}_3\text{H}_3\text{BO} + \text{H}$ -44 ± 12	
		<i>cis/trans</i> - $\text{CH}_3\text{CH}=\text{CHBO} + \text{H}$ [5] (-47 ± 10) ^b	26 ± 8 (19.0)
		$\text{CH}_2\text{CHCH}_2\text{BO} + \text{H}$ [6] (-32 ± 10) ^b	5 ± 3 (5.4)
		$\text{CH}_3\text{C}(\text{BO})\text{CH}_2 + \text{H}$ (-39 ± 10) ^b	(0.8)
		$\text{C}_2\text{H}_3\text{BO} + \text{CH}_3$ [4] -69 ± 19 (-82 ± 10) ^b	± 15 (1.9)

^aCCSD(T)/cc-pVTZ.²⁹ ^bCCSD(T)/cc-pVTZ.³⁰

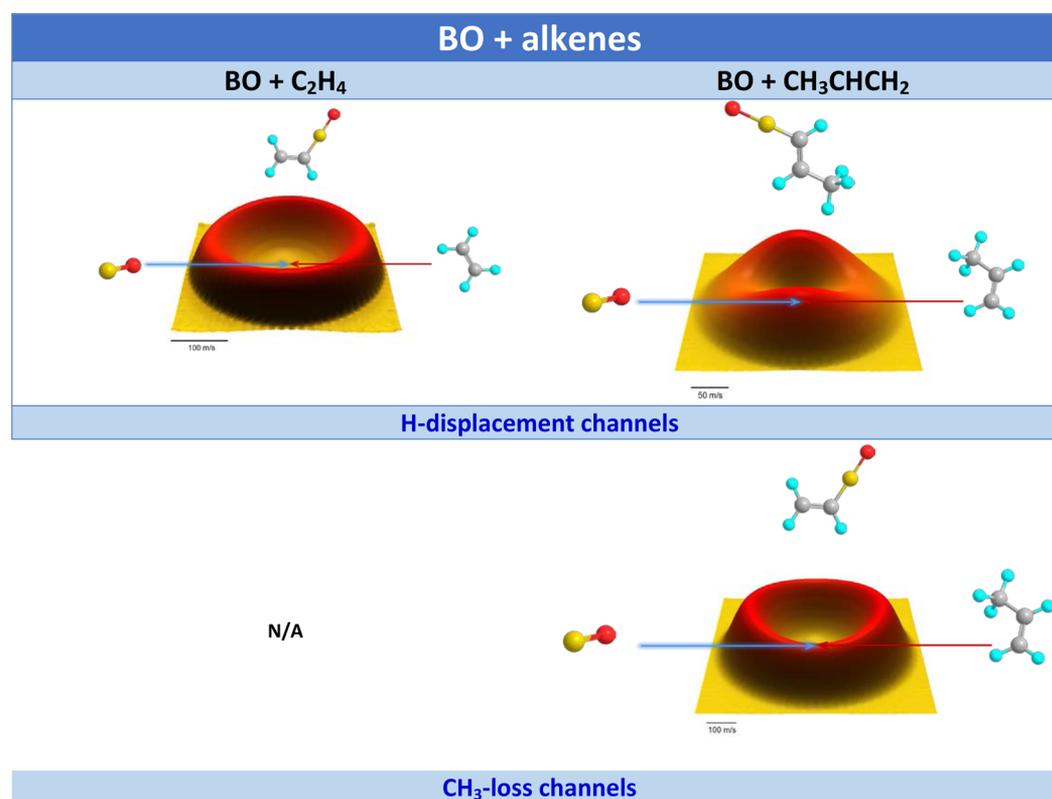


Figure 2. Flux contour map of the reactions of the boronyl radical with ethylene (H-loss) and propene (H- and CH_3 -loss).

Table 3. Summary of Key Results of the Crossed Beam Reactions of the Boron Monoxide Radical with Allene, Diacetylene, Benzene, and 1,3-Butadiene

hydrocarbon reactant	collision energy, kJ mol^{-1}	experimental (theoretical) reaction energy, kJ mol^{-1}	experimental (RRKM) branching ratio, %
H_2CCCH_2	22.0 ± 1.3	$\text{CH}_2\text{CCHBO} + \text{H}$ -53 ± 11	100
		$\text{H}_2\text{CCCHBO} + \text{H}$ [3] (-46 ± 10) ^a	(98.3)
		$\text{CH}_2(\text{BO})\text{CCH} + \text{H}$ (-29 ± 10) ^a	0 ± 15 (1.5)
		$\text{CH}_3\text{CCBO} + \text{H}$ (-74 ± 10) ^a	(0.2)
$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$	17.5 ± 0.8	$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{BO} + \text{H}$ [7] -63 ± 11 (-62 ± 10) ^b	100 (100)
C_6H_6	21.0 ± 2.0	$\text{C}_6\text{H}_5\text{BO} + \text{H}$ [8] -30 ± 12 (-37 ± 10) ^b	100 (100)
$\text{H}_2\text{CCHCHCH}_2$	23.6 ± 1.5	$\text{H}_2\text{CCHCHBO} + \text{H}$	70 ± 10
		$\text{H}_2\text{CC}(\text{BO})\text{CHCH}_2 + \text{H}$ -47 ± 14	30 ± 10
		<i>trans-Z,E</i> - $\text{H}_2\text{CCHCHBO} + \text{H}$ [9] (-45 ± 10 ; -45 ± 10) ^c	(69)
		<i>cis-Z,E</i> - $\text{H}_2\text{CCHCHBO} + \text{H}$ (-38 ± 10 ; -39 ± 10) ^c	(11)
		$\text{H}_2\text{CC}(\text{BO})\text{CHCH}_2 + \text{H}$ [10] (-38 ± 10) ^c	(20)

^aCCSD(T)-fc/cc-pVTZ.³¹ ^bCCSD(T)/CBS.³² ^cCCSD(T)-fc/cc-pVTZ.³³

ad hoc of the relevant stationary points along the minimum energy path of the underlying potential energy surface (PES). The calculations have been performed at various levels with the higher levels being CCSD(T)/cc-pVTZ and CCSD(T)/CBS by the groups of Chang,^{26,28–30,33} Mebel,^{32,34} and Bartlett.^{27,31} In addition, since these reactions are multichannel polyatomic

reactions and normally more than one set of products is possible, statistical estimates of the product branching ratios by means of the Rice–Ramsperger–Kassel–Marcus (RRKM) method have been derived to be compared with the experimental determination. The main results, as well as some information on the experimental conditions, have been concisely summarized in the

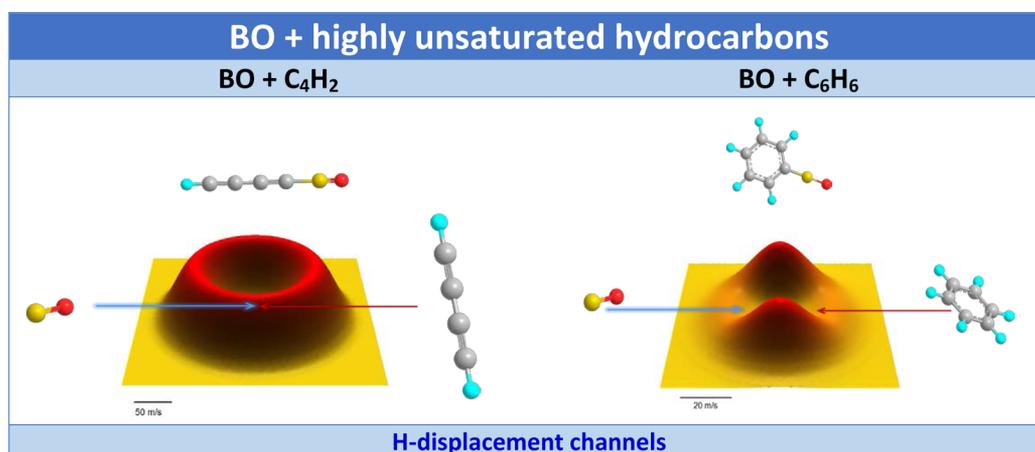


Figure 3. Flux contour map of the reactions of the boronyl radical with diacetylene and benzene (H-loss).

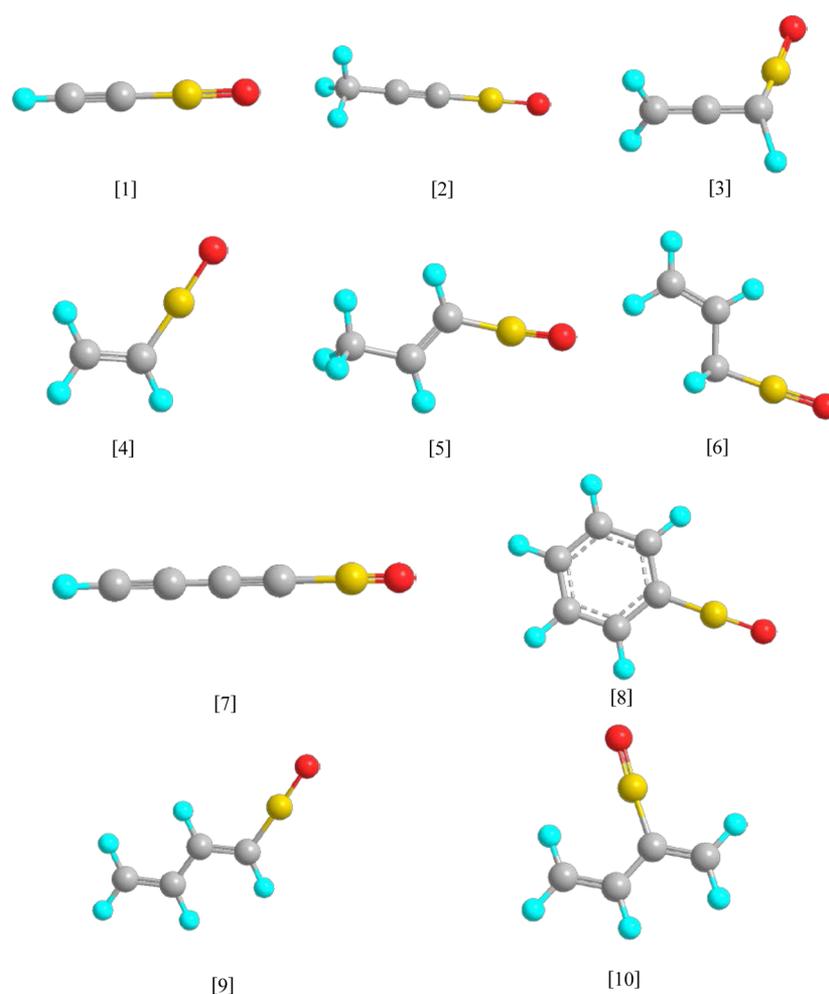


Figure 4. Structures of distinct organo boronyls experimentally identified in the reactions of boron monoxide radicals with three classes of unsaturated hydrocarbons: alkynes (1–3), olefins (4–6), and cumulenes/benzenes/dienes (7–10) (Tables 1–3); gray carbon, blue hydrogen, yellow boron, red oxygen.

Tables 1–3, while the contour maps for several systems are shown in Figures 1–3. The structures of the novel product species identified for the first time as isolated molecules are reported in Figure 4.

III.1. The $\text{BO}-\text{C}_2\text{H}_2$, $\text{BO}-\text{CH}_3\text{CCH}$, and $\text{BO}-\text{CH}_3\text{CCCH}_3$ Systems

The dynamics of the reactions of boron monoxide with acetylene,²⁶ methylacetylene,²⁷ and dimethylacetylene²⁸ share

many similarities. All reactions feature the same initial approach, with the boron monoxide diatomic radical interacting via its radical center at the boron atom with the electron density at the carbon–carbon triple bond. An addition intermediate depicting a newly formed boron–carbon bond is formed, which evolves differently in these three cases. Common to all systems, these three reactions are all barrierless and proceed via indirect

scattering dynamics as one or more bound addition intermediates are formed.

In the case of the reaction with acetylene (C_2H_2),²⁶ because of the symmetry of the acetylene molecule and hence the chemical equivalency of the carbon atoms, only one addition intermediate, HCCHBO (in two isomeric forms), can be formed on the ground doublet PES. These intermediates can only decompose via hydrogen atom emission to form the linear boronylacetylene (HCCBO) product. The only alternative mechanism involves a hydrogen migration in the initial collision complex to form the more stable OBCCH₂ intermediate, which in turn also emits atomic hydrogen forming the same linear boronylacetylene (HCCBO) molecule. While RRKM calculations indicate that the formation of boronylacetylene (HCCBO) represents the only accessible pathway, the experimental data could not distinguish explicitly between these two mechanisms because both proceed through the formation of a complex featuring alike scattering properties. According to RRKM estimates, the second mechanism accounts only for about 4% of the products, while the boronyl addition–hydrogen atom elimination pathway dominates. The center-of-mass angular distribution depicts a peak centered at about 80° suggesting that the decomposing complex has a preferential hydrogen loss direction almost parallel to the total angular momentum vector. This is also confirmed by the geometry of the tight exit transition state derived by electronic structure calculations.

Considering the reaction of the boronyl radical with methylacetylene,²⁷ the symmetry of the boronyl radical attack is removed, and the addition can occur on either the C1 or C2 sites. Quite interestingly, the electronic structure calculations pointed out that a van der Waals complex located 17 kJ mol⁻¹ below the separated reactants is formed in the entrance channel with the boron side of the boronyl radical interacting almost equivalently with the C1 and C2 atoms of the methylacetylene reactant. A submerged barrier of 7 kJ mol⁻¹ has to be surmounted to form the C2 addition intermediate, while a submerged barrier of only 2 kJ mol⁻¹ connects the van der Waals well to the C1 addition intermediate located at 197 kJ mol⁻¹ below the reactants asymptote. The C1 addition is, therefore, favored. The resulting C₃H₄BO doublet radical intermediates undergo unimolecular decomposition involving three competing reaction mechanisms via two distinct atomic hydrogen losses and a methyl group elimination. Two isomeric products are formed in the hydrogen loss channels, that is, 1-propynyl boron monoxide (CH₃CCBO) if the acetylenic hydrogen atom is emitted from C1 of the CH₃CCHBO intermediate or propadienyl boron monoxide (CH₂CCHBO) if the hydrogen atom is ejected from the methyl group. Experiments with the partially deuterated reactants CD₃CCH and CH₃CCD were performed. According to those results, the hydrogen loss from the acetylenic carbon atom (C1) is by far the dominant channel with a ratio of about 0.9:0.1. Addition of boronyl radical to the C1 of methylacetylene followed by the migration of the boronyl group to the C2 carbon atom or an initial addition of BO to the sterically less favorable C2 carbon atom of methylacetylene are also possible and lead, by loss of a methyl group, to the boronylacetylene (HCCBO). The experimentally deduced branching ratios of the channels forming CH₂CCHBO, CH₃CCBO, and HCCBO are 4% ± 3%, 40% ± 5%, and 56% ± 15%, respectively. These results are in excellent agreement with the RRKM calculations of the product branching ratio (1%, 38%, and 61%, respectively). Experimentally, some propensity for sideways scattering for the hydrogen displacement channel was observed, which suggests that the hydrogen atom

leaves perpendicularly to the rotational plane of the decomposing complex and almost parallel to the total angular momentum vector. The overall energy budget and the fraction of energy released as product translational energy are essentially in line with the 1-propynyl boron monoxide (CH₃CCBO) formation channel, and only a minor contribution can come from propadienyl boron monoxide (CH₂CCHBO). The methyl loss channel is the dominant one, according to both experimental and theoretical determination. The peak of the center-of-mass product translational distribution is well displaced from zero translational energy thus denoting the presence of a tight transition state in the exit channel. For this channel, the center-of-mass angular distribution is backward–forward symmetric with some polarization. This last feature is quite typical of methyl loss channels when compared to hydrogen displacement pathways.^{35,36}

Finally, in the reaction of boron monoxide with dimethylacetylene,²⁸ the reaction is initiated by the addition of the boronyl with the radical center located at the boron atom to the π -electron density at the acetylenic carbon–carbon triple bond without entrance barrier leading to form *cis,trans*-C₄H₆BO doublet radical intermediates. As in the case of the reaction with acetylene, the boronyl radical attack is now “symmetric”. The *cis*-C₄H₆BO addition isomer easily undergoes *cis*–*trans* isomerization; the *trans*-C₄H₆BO isomer was found to follow unimolecular decomposition by losing a methyl group (CH₃) thus forming 1-propynyl boron monoxide (CH₃CCBO). For this system, there was no experimental evidence of atomic or molecular hydrogen elimination. The near exclusiveness of the methyl loss pathway is confirmed by the accompanying computational study of the stationary points of the PES and RRKM estimates, which predict that the methyl group loss channel is by far the dominant one (99.99%) with the atomic hydrogen loss channel accounting only for 0.01% of the global reaction. The contour maps of the three systems are comparatively reported in Figure 1.

III.2. The BO–C₂H₄ and BO–CH₃CHCH₂ Systems

Also in the case of the reaction with alkenes, the initial interaction features the attack of the boronyl radical to the π bond of each olefin with the formation of bound doublet radical intermediates, which then decompose into products. With respect to the reaction with ethylene,²⁹ the symmetric boronyl radical addition leads to a doublet radical intermediate (CH₂CH₂BO), which either undergoes unimolecular decomposition through hydrogen atom emission from the C1 atom forming vinyl boron monoxide (C₂H₃BO) or isomerizes via a hydrogen shift to the CH₃CHBO radical, which can then lose a hydrogen atom from the C1 atom forming again the same molecular product, vinyl boron monoxide (C₂H₃BO). Similarly to the acetylene reaction, experimentally it was not possible to distinguish between these two competing micromechanisms, because the characteristics of both product translational energy distributions (in particular the peak position) and the slight propensity for sideways scattering in the center-of-mass angular distribution are compatible with the characteristics of both transition states leading from the two intermediates CH₂CH₂BO/CH₃CHBO to the products. Here, RRKM calculations demonstrated that under the experimental conditions of the CMB experiment about 44% of the products are formed via the hydrogen atom elimination from the initial addition intermediate CH₂CH₂BO and 56% via the hydrogen loss from CH₃CHBO via rather tight exit transition states.

Considering the BO–propene system,³⁰ the asymmetric barrierless addition of the boron monoxide radical involves

either the terminal carbon atom (C1) or the central carbon atom (C2) of propene, forming two doublet radical intermediates, $\text{CH}_3\text{CHCH}_2\text{BO}$ and $\text{CH}_3\text{CH}(\text{BO})\text{CH}_2$, respectively. The long-lived $\text{CH}_3\text{CHCH}_2\text{BO}$ intermediate can undergo unimolecular decomposition via an atomic hydrogen loss from the vinyl group or an atomic hydrogen ejection from the methyl group leading to the formation of the molecular products *cis/trans*-1-propenyl-oxo-borane (CH_3CHCHBO) and 3-propenyl-oxo-borane ($\text{CH}_2\text{CHCH}_2\text{BO}$), respectively. The $\text{CH}_3\text{CHCH}_2\text{BO}$ intermediate can also isomerize via hydrogen atom shift to $\text{CH}_3\text{CH}_2\text{CHBO}$, which, in turn, decomposes by hydrogen atom emission to *cis/trans*- CH_3CHCHBO or by CH_3 elimination to vinyl boron monoxide (CH_2CHBO). The $\text{CH}_3\text{CH}(\text{BO})\text{CH}_2$ intermediate, which can be formed either via the addition of the boron monoxide radical to the central carbon atom of propene or via a 1,2-BO migration from $\text{CH}_3\text{CHCH}_2\text{BO}$, can undergo two competing unimolecular decomposition pathways via either an atomic hydrogen elimination from the C2 carbon atom to form $\text{CH}_3\text{C}(\text{BO})\text{CH}_2$ or methyl group elimination to yield CH_2CHBO . Experiments using partially deuterated propylenes (CD_3CHCH_2 and $\text{CH}_3\text{C}(\text{D})\text{CD}_2$) revealed that the loss of a vinyl hydrogen atom is the dominant hydrogen elimination pathway ($85\% \pm 10\%$) forming *cis/trans*-1-propenyl-oxo-borane, while the loss of a methyl hydrogen atom leading to 3-propenyl-oxo-borane accounts for only $15\% \pm 10\%$. The experimental branching ratio for the vinyl hydrogen atom loss, methyl hydrogen atom loss, and methyl group loss are $(26\% \pm 8\%):(5\% \pm 3\%):(69\% \pm 15\%)$. The experimental data are in agreement with the RRKM branching ratio of 19%:5%:75%, respectively, while about 1% is associated with the formation of the third isomer $\text{CH}_3\text{C}(\text{BO})\text{CH}_2$. To be noted that the RRKM branching ratios were calculated considering an initial 100% population of either $\text{CH}_3\text{CHCH}_2\text{BO}$ or $\text{CH}_3\text{CH}(\text{BO})\text{CH}_2$; due to the fast interconversion, the calculated branching ratios of the products remain the same in both cases. Finally, the experimentally observed propensity for sideways scattering in the hydrogen displacement channels is perfectly in line with the geometry of the decomposing transition states involved, while the methyl loss channel is associated with a more polarized backward–forward symmetric center-of-mass angular distribution. The contour maps of the two systems are comparatively reported in Figure 2.

III.3. The $\text{BO}-\text{CH}_2\text{CCH}_2$, $\text{BO}-\text{C}_4\text{H}_2$, $\text{BO}-1,3-\text{CH}_2\text{CHCH}_2$, and $\text{BO}-\text{C}_6\text{H}_6$ Systems

In the case of the reaction with allene,³¹ once again the boron monoxide radical interacts with the π electron density without any entrance barrier to form the $\text{CH}_2\text{CCH}_2(\text{BO})$ intermediate via addition to one of the terminal carbon atoms or the more stable intermediate $\text{CH}_2\text{C}(\text{BO})\text{CH}_2$ through addition to the central carbon of the allene molecule. The formation of a shallow van der Waals complex precedes these additions. The $\text{CH}_2\text{CCH}_2(\text{BO})$ and $\text{CH}_2\text{C}(\text{BO})\text{CH}_2$ intermediates can easily isomerize one to the other because of a small energy barrier associated with isomerization via migration of the BO moiety. Then, the $\text{H}_2\text{CCCH}_2(\text{BO})$ complex can undergo two competing unimolecular decomposition pathways via atomic hydrogen loss from the C3 and C1 carbon atoms of the allene moiety to form 3-propynyl-oxoborane ($\text{CH}_2(\text{BO})\text{CCH}$) and propadienyl-oxoborane (boronyllallene, CH_2CCHBO), respectively. The $\text{CH}_2\text{C}(\text{BO})\text{CH}_2$ intermediate is significantly more stable than $\text{CH}_2\text{CCH}_2(\text{BO})$ due to the resonance stabilization of the allyl moiety. There are no fission pathways from this intermediate, the destiny of which is

isomerization to other bound intermediates. Among the possible isomerization, the one leading to $\text{CH}_2\text{CCH}_2(\text{BO})$ is by far the favorite one. In principle, after several rearrangements, the system can access the same potential energy surface of the $\text{BO}-\text{CH}_3\text{CCH}$ system. The conducted experiments, however, demonstrated that the methyl loss channel is closed, and indeed, statistical RRKM calculations fully support these suggestions, with boronyllallene being the major product (98.3%), while 3-propynyl-oxoborane ($\text{CH}_2(\text{BO})\text{CCH}$) and 1-propynyl-oxoborane (CH_3CCBO) have a yield of only 1.5% and 0.2%, respectively. Finally, the marked preference for sideways scattering observed in the experimental center-of-mass angular distributions nicely correlates with the geometry of the decomposing transition state connecting the initial addition intermediate $\text{CH}_2\text{CCH}_2(\text{BO})$ to boronyllallene ($\text{CH}_2\text{CCH}(\text{BO})$).

Considering the diacetylene reactant,³² boron monoxide interacts with one of the carbon–carbon triple bonds of the highly symmetric diacetylene molecule, adding at one of the terminal carbon atoms in a barrierless process. This leads to the doublet radical intermediate (HC_4HBO), which then undergoes unimolecular decomposition through hydrogen atom emission from the C1 carbon atom via a tight exit transition state forming the boronyldiacetylene molecule (HCCCCBO). The potential energy surface calculations identified five alternative reaction pathways to boronyldiacetylene formation, but RRKM calculations predict that at the collision energy of the experiment, about 94% of boronyldiacetylene originates from the initial HC_4HBO collision complex, whereas about 5% is formed after a hydrogen shift from the C1 carbon atom to the boron atom. The center-of-mass angular distribution is isotropic, a fact that indicates a weakly polarized system suggesting that the initial orbital angular momentum does not couple well with the final orbital angular momentum as the light hydrogen atom cannot carry away much orbital angular momentum and most of the initial angular momentum is therefore channeled into the rotational degrees of freedom of the linear boronyldiacetylene product (HCCCCBO).

The reaction of the boron monoxide radical with 1,3-butadiene³³ features the barrierless addition of the boron monoxide radical to the terminal carbon atom (C1/C4) or to the central carbon atom (C2/C3) of 1,3-butadiene. The resulting long-lived BOC_4H_6 intermediate(s) undergo isomerization or unimolecular decomposition with at least two distinct H-loss pathways open and leading to 1,3-butadienyl-1-oxoboranes ($\text{CH}_2\text{CHCHCHBO}$) and 1,3-butadienyl-2-oxoboranes ($\text{CH}_2\text{C}(\text{BO})\text{CHCH}_2$). Experiments with partially deuterated D2- and D4-1,3-butadiene demonstrated that the hydrogen loss from the methylene moiety (CH_2) dominates with a yield of $70\% \pm 10\%$, while the hydrogen emission from the methylidyne group (CH) accounts for only $30\% \pm 10\%$. The experimental data agree nicely with the theoretically predicted branching ratio of 80% and 19%. Also for this reaction, the marked preference for sideways scattering observed in the experimental center-of-mass angular distributions nicely correlates with the geometry of the decomposing transition states.

Finally, in the reaction with benzene, a weakly bound van der Waals complex is formed with the boron atom of the boron monoxide radical interacting with the aromatic ring.³⁴ The complex easily isomerizes over a transition state residing 4 kJ mol^{-1} below the energy of the reactants via addition of the boronyl radical with its boron atom to the benzene ring to form the $\text{C}_6\text{H}_6\text{BO}$ addition intermediate, which resides in a deep potential energy. The products phenyl oxoborane ($\text{C}_6\text{H}_5\text{BO}$) plus atomic hydrogen

can be formed via emission of the hydrogen atom bound to the same carbon atom as the boronyl group through a tight exit barrier. A rather exotic but competing reaction channel involves an isomerization via a hydrogen shift from the carbon to the boron atom. Also in this case, the only possible product is phenyl oxoborane via atomic hydrogen loss from the boron atom. For this reaction, a strong bias for sideways scattering has been observed, which suggests that the hydrogen atom leaves the decomposing complex almost perpendicularly to the rotational plane of the fragmenting complex. By analyzing the structures of the two transition states involved, it is possible to infer that the first route, connecting the addition intermediate to the phenyl oxoborane product, is the dominant one because it is the only case where the hydrogen atom is emitted perpendicularly to the scattering plane. The RRKM calculations at the collision energy of experiment corroborate this, as they provide evidence that 85% of the phenyl oxoborane is formed from the first addition intermediate, whereas 15% is produced after isomerization via a hydrogen shift from the carbon to the boron atom (Figure 3).

IV. DISCUSSION AND CONCLUSIONS

By analyzing the reaction mechanism, involved collision complexes, and products of the boron monoxide radical reactions with the unsaturated C2–C6 hydrocarbon molecules acting as simplest representatives of acetylenes, olefins, and aromatics along with their substituted and conjugated counterparts, we can draw important general conclusions on the reactivity of boronyl (BO) with unsaturated substrates. In all cases, the boronyl radical adds to the electron rich π electronic system of the unsaturated or aromatic hydrocarbon with the radical center located at the boron center. These addition pathways do not involve any entrance barrier and lead to the formation of a carbon–boron single bond. The initially formed doublet radical collision complexes either decompose via atomic hydrogen or methyl group loss or undergo hydrogen migration prior to their unimolecular decomposition. With the exception of the dimethylacetylene reactant, in all cases the boron monoxide radical versus atomic hydrogen exchange mechanism was open leading to highly unsaturated isolated organoboronyl monomers (Figure 4), which cannot trimerize under single collision conditions. Besides the hydrogen loss pathway, methylacetylene, dimethylacetylene, and propylene, those reactants carrying one or two methyl groups, were also found to eliminate a methyl group. A consistent trend suggests that all exit transition states are rather tight with those involved in the hydrogen atom loss depicting exit barriers of typically 25–35 kJ mol⁻¹, whereas the methyl loss pathways are associated with tighter exit transition states located about 30–50 kJ mol⁻¹ above the separated products. Further, the overall energetics suggest that those bimolecular reactions are exoergic by 40–90 kJ mol⁻¹; likewise all transition state involved in the isomerization and hydrogen/methyl losses are located below the energy of the separated reactants suggesting that these reactions also occur at ultralow temperatures. Therefore, all findings fully confirm that this reaction class leads to the formation of highly unsaturated organo boronyl molecules. We also identified multiple doublet radical intermediates; under single collision conditions, the latter cannot be stabilized, but in higher density environments such as in boron-based combustion systems, these intermediates can be stabilized and hence can effectively take part in a rich organo boron chemistry. Based on a recommendation by Pyykko³⁷ on the nature of multiple bonds, the boron–oxygen bonds of all boronyls illustrated here should be considered as triple bond, as they are shorter than 135 pm, a distance identified as

representative of a boron–oxygen double bond. The extracted generalized concepts of a barrierless addition–hydrogen/methyl elimination and overall exoergic reaction are now being applied to elucidate the reaction dynamics of hitherto even more exotic systems: the formation of organic boronyl sulfides (RBS).^{38,39} The reactions of the isovalent boronyl sulfide radical (BS) are conducted with unsaturated hydrocarbons such as acetylene and ethylene under single collision conditions accessing the previously elusive class of boronyl sulfides under collisionless conditions thus exploring the class of strange, new boronyl sulfides.

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Funding

This work was supported by the Air Force Office of Scientific Research (Grant FA9550-12-1-0213). N.B. acknowledges partial support from “Fondazione Cassa di Risparmio di Perugia (Progetto 2014.0253.021 Ricerca Scientifica e Tecnologica)”.

Notes

The authors declare no competing financial interest.

Biographies

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