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Gas-Phase Synthesis of Phenyl Oxoborane (C_6H_5BO) via the Reaction of Boron Monoxide with Benzene

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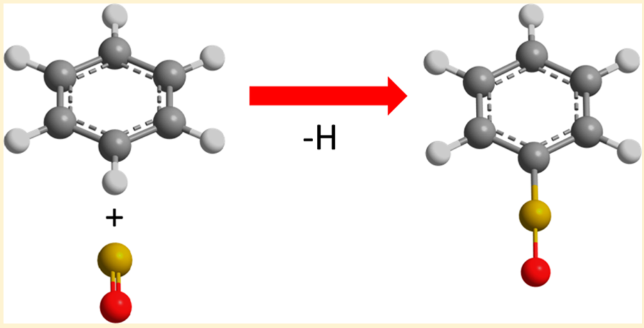
Ⓢ *Supporting Information*

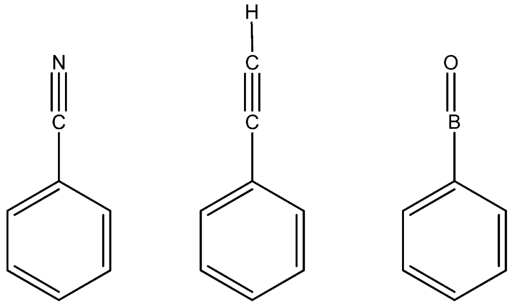
ABSTRACT: Organyl oxoboranes (RBO) are valuable reagents in organic synthesis due to their role in Suzuki coupling reactions. However, organyl oxoboranes (RBO) are only found in trimeric forms (RBO_3) commonly known as boronic acids or boroxins; obtaining their monomers has proved a complex endeavor. Here, we demonstrate an oligomerization-free formation of organyl oxoborane (RBO) monomers in the gas phase by a radical substitution reaction under single-collision conditions in the gas phase. Using the cross molecular beams technique, phenyl oxoborane (C_6H_5BO) is formed through the reaction of boronyl radicals (BO) with benzene (C_6H_6). The reaction is indirect, initially forming a van der Waals complex that isomerizes below the energy of the reactants and eventually forming phenyl oxoborane by hydrogen emission in an overall exoergic radical−hydrogen atom exchange mechanism.



INTRODUCTION

In 1936, Kinney and Pontz discovered that organyl oxoboranes (RBO) exist in cyclotrimeric forms ($(RBO)_3$) commonly known as boronic acids or boroxins.[1] However, the isolation of the corresponding monomers in the gas phase has been highly elusive but extensively sought by the organic synthesis community due to their invaluable role as reagents in, for example, Suzuki cross-coupling reactions.[2] Phenyl oxoborane (**3**; C_6H_5BO) (Scheme 1) was isolated in an argon matrix and identified via infrared (IR) spectroscopy after its generation via flash pyrolysis of the corresponding boroxine.[3] Further, the role of boronyl (BO) as a ligand has been consistently investigated[4] using a range of platinum coordination centers, where recent advances have led to the formation of a complex immune to oligomerization.[5] The use of Lewis acid stabilization has also been successful in isolating a condensate with only one BO ligand.[6] Another hitherto uninvestigated route to phenyl oxoborane monomers involves a free radical substitution reaction (S_R) of aromatic hydrocarbons such as benzene by exploiting the crossed molecular beams method under single-collision conditions in the gas phase (reaction 1).[7]

Scheme 1



[1] [2] [3]

$$C_6H_6 + X \rightarrow C_6H_5X + H \qquad (1)$$

The reactions of benzene with the cyano (CN)[8] and ethynyl radicals (CCH),[9] which are isoelectronic with the boronyl radical (BO), have been explored using this technique. These barrierless radical−neutral reactions are initialized by an addition of the radical to the benzene ring followed by emission of a hydrogen atom to form cyanobenzene (**1**) and phenylacetylene (**2**) in overall exoergic reactions (Scheme 1).[8,9]

The boron monoxide radical (BO) is isoelectronic with the cyano (CN) and the ethynyl (CCH), sharing characteristic high bond strengths (799, 749, and 728 kJ mol^{-1}), polarizabilities

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(146, 141, and 139 Å^3), and electron affinities (2.83, 3.86, and 2.97 eV) and similar chemical reactivities with acetylene[10] and ethylene.[11] Here, we show that phenyl oxoborane (C_6H_5BO) (**3**) can be formed in the gas phase via a facile and exoergic reaction between benzene (C_6H_6) and boron monoxide (BO) involving a radical substitution mechanism (reaction 1).

■ RESULTS

Experimental Results. Reactive scattering signals were observed at *m*/*z* 104 (strong) and *m*/*z* 103 (weak). The signal at *m*/*z* 104 corresponds to the formation of a product with the molecular formula $C_6H_5{}^{11}BO$ formed via the boronyl versus atomic hydrogen exchange channel. The signal at *m*/*z* 103 could originate from molecular hydrogen loss to form $C_6H_4{}^{11}BO$, from the $C_6H_5{}^{10}BO$ species, from dissociative ionization of the $C_6H_5{}^{11}BO$ product in the electron impact ionizer, or from a combination of these channels. The signal at *m*/*z* 103 was found to have an identical time of flight (TOF) profile as the signal at *m*/*z* 104 with an intensity of only about 20%; this intensity is in line with the natural $^{10}B/^{11}B$ isotope abundances, and therefore, the signal recorded at both masses can be attributed to the formation of C_6H_5BO. Figure 1 depicts the experimental data: the laboratory angular distribution (upper) and three typical TOFs (lower) recorded at *m*/*z* 104. The circles present the experimental data and the lines the best fit utilizing the mass combination of the products of 104 and 1 amu. Note that the laboratory angular distribution peaks at the center of mass (CM) angle of 47° is nearly symmetric around the center of mass and extends to about 30°; these findings suggest indirect scattering dynamics via the formation of $C_6H_6{}^{11}BO$ complex(es).

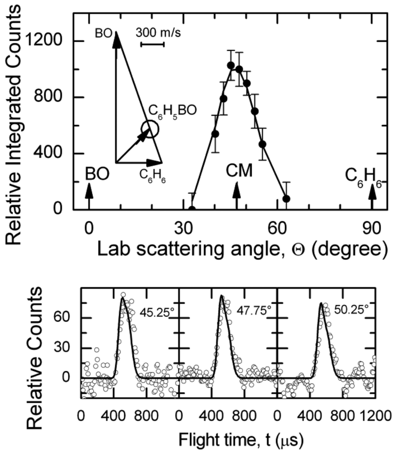

Figure 1. Laboratory angular distribution (upper) and time of flight spectra (lower) of reactively scattered species recorded at mass to charge (*m*/*z*) 104 ($C_6H_5{}^{11}BO$) in the reaction of boron monoxide radicals with benzene molecules. The circles represent the experimental data, the solid line represents the best fit to the data, and CM designates the center of mass angle.

Information on the reaction mechanism is gained by moving from the laboratory to the center of mass (CM) reference frame utilizing a forward-convolution routine.[7] The CM functions generated by this approach are depicted in Figure 2 as the product angular ($T(\theta)$, upper) and translational energy distributions ($P(E'_T)$, lower). The best-fit product translational energy distribution $P(E'_T)$ peaks at 10 ± 5 kJ mol^{-1} and is characterized by a tail which extends up to 51 ± 10 kJ mol^{-1} (Figure 2). By subtracting the collision energy from the maximum product translational energy, we obtain a reaction energy of 30 ± 12 kJ mol^{-1} for the formation of a product with the molecular formula $C_6H_5{}^{11}BO$. Also, we find that about 29 ± 5% of the total available energy of the reaction products is released into translational degrees of freedom, indicating indirect scattering dynamics.[7] Finally, the distribution peaks away from zero translational energy at around 10 kJ mol^{-1}. This finding suggests the existence of a tight exit transition state.

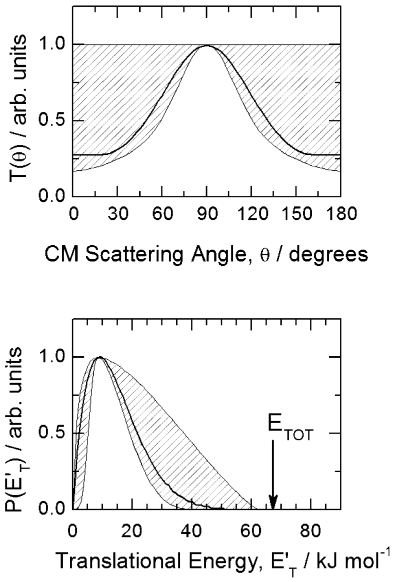

Figure 2. Center of mass translational energy flux distribution (lower) and angular flux distribution (upper) for the hydrogen atom loss channel in the reaction of boron monoxide with benzene leading to the $C_6H_5{}^{11}BO$ product. Hatched areas indicate the acceptable upper and lower limits of the fits accounting for the error limits, and solid lines define the best-fit function.

Let us turn now to the center of mass angular distribution. The CM angular distribution exhibits intensity over the complete angular range and is forward–backward symmetric. These findings indicate that the reaction involves an indirect (complex-forming) reaction mechanism via $C_6H_6{}^{11}BO$ intermediate(s) with lifetimes longer than the(ir) rotation period(s). Further, the best fit depicts a distribution maximum at 90°. This "sideways scattering" suggests geometrical constraints when the $C_6H_6{}^{11}BO$ complex(es) fragment via hydrogen loss. Specifically, the data propose that the atomic hydrogen is lost almost perpendicularly to the rotation plane of the decomposing complex almost parallel to the total angular momentum vector.[6,7]

Theoretical Results. To address the question "Which is the dominant reaction pathway and what are the final product(s) in the reaction of the boron monoxide radical with benzene?", we will compare the experimental results to the electronic structure calculations on the C_6H_6BO potential energy surface (Figure 3). The optimized Cartesian coordinates, numbers of imaginary frequencies, and total energies of various reactants, products, reaction intermediates, and transition states are available in the Supporting Information. These computations predict that, upon approach of the reactants, the weakly bound van der Waals complex **i1** is formed; this complex resides only 9 kJ mol^{-1} below the energy of the separated reactants. Intermediate **i1** isomerizes over a transition state residing 4 kJ mol^{-1} below the energy of the reactants via addition of the boronyl radical

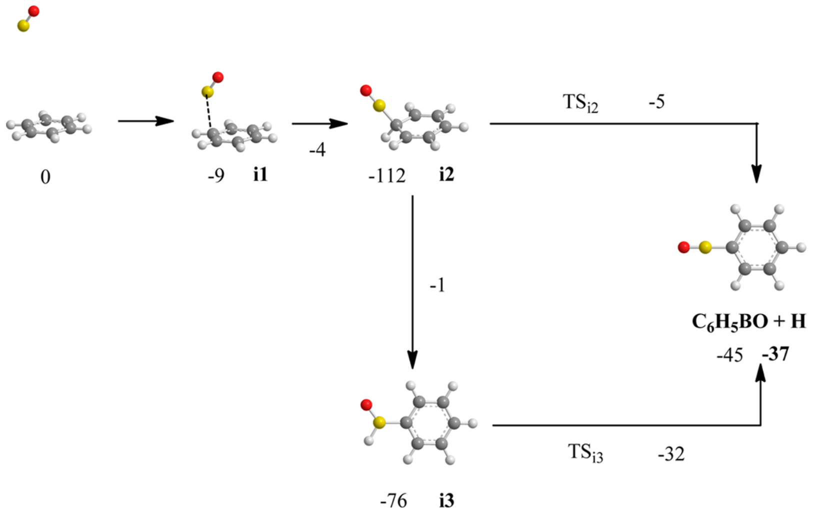

Figure 3. Schematic representation of the lowest energy pathways on the $C_6H_6{}^{11}BO$ potential energy surface (PES) in the reaction of boron monoxide (^{11}BO) and benzene (C_6H_6) leading to phenyl oxoborane ($C_6H_5{}^{11}BO$). All energies are given in kJ mol^{-1} relative to the reactant energies. Roman and boldface numbers show relative energies computed at the G3(MP2,CC) and CCSD(T)/CBS levels of theory, respectively. Atom designations: boron (yellow), oxygen (red), carbon (gray), and hydrogen (white).

with its boron atom to the benzene ring to form reaction intermediate **i2**. The latter resides in a deep potential energy well of 112 kJ mol^{-1}. From here, phenyl oxoborane (C_6H_5BO) 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 located 40 kJ mol^{-1} above the energy of the separated products. The overall reaction was found to be exoergic by 45 kJ mol^{-1} at the G3(MP2,CC) level of theory and by 37 kJ mol^{-1} at the most accurate CCSD(T)/CBS level. This pathway from the reactants via **i2** to the products presents a prototypical example of a radical substitution reaction (S_R) under single-collision conditions in the gas phase. It further represents the lowest energy pathway to phenyl oxoborane (C_6H_5BO). A competing reaction channel involves an isomerization from **i2** to **i3** via a hydrogen shift from carbon to boron. From **i3**, phenyl oxoborane (C_6H_5BO) is accessed via atomic hydrogen loss from the boron atom through a tight exit transition state that is 13 kJ mol^{-1} above the energy of the separated products. It should be noted that intermediate **i2** can isomerize to itself by migration of the BO group from one carbon atom to the neighboring one via a bicyclic transition state located 82 kJ mol^{-1} higher in energy than **i2**.

■ DISCUSSION

We shall now combine our experimental findings with the computations to elucidate the actual reaction pathway(s). First, we observed a product with *m/z* 104, which corresponds to a product with the formula $C_6H_5{}^{11}BO$. Here, the experimentally determined exoergicity of the reaction to form atomic hydrogen plus the phenyl oxoborane (C_6H_5BO) molecule of 30 ± 12 kJ mol^{-1} agrees nicely with the computed reaction energies of 45 kJ mol^{-1} (G3(MP2,CC)) and 37 kJ mol^{-1} (CCSD(T)/CBS). The formation of the phenyl isooxoborane product (C_6H_5OB) is endoergic by 223 kJ mol^{-1}, and hence, it cannot be formed in our experiment considering a collision energy of only 21 ± 2 kJ mol^{-1}. Therefore, we have established that phenyl oxoborane (C_6H_5BO) (104 amu) presents the sole reaction product. We stress that the reactions were conducted under single-collision conditions in the gas phase, meaning that the product formed flies *undisturbed*, i.e. without di- or trimerization, to the detector. These single-collision conditions present the unique advantage of single bimolecular reaction events, which cannot be provided in classical matrix isolation experiments. Consequently, crossed beam experiments only synthesize and detect the monomer of phenyl oxoborane.[12]

Which is the dominating reaction pathway to form phenyl oxoborane (C_6H_5BO): **i1** → **i2** or **i1** → **i2** → **i3** (Figure 3)? Both reaction pathways depict tight exit transition states involving barriers of 40 and 13 kJ mol^{-1}, respectively. The existence of a tight exit transition state was also predicted on the basis of the off-zero peaking of the center of mass translational energy distribution. However, the distribution maximum of the center of mass angular distribution delivers the most valuable insight into the reaction pathway. This finding suggests that the hydrogen atom leaves the decomposing complex almost perpendicularly to the rotational plane of the decomposing complex. Here, the exit transition state from **i2** to the products (Figure 4) depicts a decomposing collision complex with a hydrogen emission direction as denoted by the dashed line perpendicular to the plane of the molecule and parallel to the *C* axis. Grice and Smith,[13] using microcanonical transition state theory, demonstrated that for a reaction intermediate formed in a supersonic expansion that undergoes atomic hydrogen emission through an exit barrier and parallel to one of the principal rotation axis will cause a strong peaking of $T(\theta)$ at 90°. Our experiment fits into the premises of this

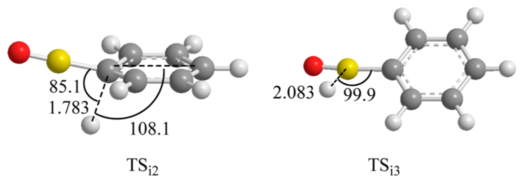

Figure 4. Schematic representation of the transition state structures **TSi2** and **TSi3** on the $C_6H_6{}^{11}BO$ potential energy surface (PES) in the reaction of boron monoxide (^{11}BO) and benzene (C_6H_6) leading to phenyl oxoborane ($C_6H_5{}^{11}BO$). Angles are in degrees and distances in angstroms.

model, including a hydrogen emission at 108° (Figure 4) and the existence of an exit barrier. If we compare the alternative transition state structure from **i3** to the products as seen in Figure 4, we find the emission direction is from the boronyl group, which could rotate freely; this in turn would result in an isotropic angular distribution, which is clearly not observed. On the basis of these findings we conclude that phenyl oxoborane (C_6H_5BO) is predominantly formed through hydrogen emission from **i2** rather than from **i3**. In fact, statistical (RRKM) calculations at the collision energy of 21 kJ mol^{-1} provide evidence that 85% of the phenyl oxoborane (C_6H_5BO) is formed from **i2**, whereas 15% is produced via **i3**. These observations are comparable to previous experiments using isoelectronic reactants cyanide[8] and ethynyl[9] radicals, respectively, which also exhibit "sideways" scattering.

CONCLUSION

In summary, we have established a directed synthesis of the phenyl oxoborane monomer (C_6H_5BO) in the gas phase under single-collision conditions. This presents the simplest prototype example of a radical substitution (S_R) reaction involving the boronyl radical (BO) reactant. The reaction of the boronyl radical with benzene proceeds via a submerged barrier involving a van der Waals complex, is overall exoergic, and is dictated by a boronyl versus hydrogen atom exchange. The facile route to form aromatic boronyl species can be considered as a benchmark study to synthesize hitherto elusive boronyl-substituted aromatic species via radical substitution (S_R) reactions.

EXPERIMENTAL SECTION

Experimental Methods. We performed a crossed molecular beam experiment by crossing a well-defined pulsed boron monoxide (BO) molecular beam with a pulsed argon-seeded benzene beam at fractions of 0.1% at a collision energy, E_c, of 21 ± 2 kJ mol^{-1}.[7,10] A molecular beam of boron monoxide radicals was generated by seeding laser-ablated boron from a boron rod in carbon dioxide, which acted as both a seeding and reactant gas.[10] Boron monoxide is formed via abstraction of atomic oxygen from carbon dioxide, giving carbon monoxide as a byproduct; note that neither carbon dioxide nor carbon monoxide react with the benzene molecule. The beam contains two reactive species: boron monoxide and atomic boron. As demonstrated earlier, the reaction of atomic boron with benzene yields a $^{11}BC_6H_5$ product (88 amu),[14] which is lighter than the potential $^{11}BOC_6H_x$ products; therefore, the presence of atomic boron does not interfere with the interpretation of the data from the reaction of boron monoxide with benzene. After passing through a skimmer to the reaction chamber, a four-slot chopper wheel selected a specific segment of the pulsed beam with a well-defined peak velocity (vp =1750 ± 30 ms^{-1}) and speed ratio (S = 2.7 ± 0.3). The boron monoxide radical beam (BO) then crossed a pulsed benzene (C_6H_6) beam (v_p = 610 ± 20 ms^{-1}, S = 12.0 ± 0.3) perpendicularly in the interaction region at a collision energy of 21 ± 2 kJ mol^{-1}. The reaction products were analyzed by a rotatable mass spectrometer operated in the time of flight mode and ionized via electron impact at 80 eV; the ions passed a quadrupole mass filter and reached a Daly type ion counter. After the TOF spectra were recorded at multiple angles, these data were integrated to obtain the laboratory angular distribution. A forward-convolution routine was used to fit the experimental data and to convert from the laboratory to the center of mass frame for analysis.[7]

Theoretical Methods. The hybrid density functional B3LYP[15] with the 6-311G(d,p) basis set was used to calculate the critical points (reactants, intermediates, transition states, and products) on the $C_6H_6{}^{11}BO$ potential energy surface (PES) in the reaction of ^{11}BO with benzene. At this level of theory, optimized Cartesian coordinates, unscaled vibrational frequencies, moments of inertia, and zero-point energies (ZPE) were also obtained. The optimized Cartesian coordinates of all species were used for single-point G3(MP2,CC) calculations aimed at obtaining more accurate relative energies.[16,17] For the reactants and products, we additionally performed coupled cluster CCSD(T) calculations[18] with Dunning's correlation-consistent cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets,[19] with extrapolation of the total energies to the complete basis set (CBS) limit.[20] The B3LYP and CCSD(T) calculations were carried out using the GAUSSIAN 09[21] and MOLPRO 2010[22] program packages. It should be noted that the B3LYP approach is commonly accepted to provide reliable geometries, especially for molecules containing only first-row elements, with the accuracy in bond lengths and angles being within 0.01 Å and 1°, respectively.[20] In our earlier works on similar reaction systems, we also demonstrated that B3LYP optimized structures normally agree closely with geometries optimized at the higher QCISD and CCSD(T) theoretical levels.[21,22] The single-point G3(MP2,CC) relative energies computed at the B3LYP/6-311G** optimized structures are expected to be accurate within ±10 kJ mol^{-1}, whereas the CCSD(T)/CBS energies of the reaction products should have an accuracy of ±5 kJ mol^{-1}. Rate constants $k(E)$ were calculated using RRKM theory,[23−25] where they were treated as functions of the internal energy, which was taken as a sum of the energy of chemical activation in the C_6H_6 + BO reaction and a collision energy, assuming that a dominant fraction of the latter is converted to the internal vibrational energy. The harmonic approximation was employed for calculating the total number and density of states. Product branching ratios were computed by solving first-order kinetic equations for unimolecular reactions according to the kinetics scheme devised from the ab initio potential energy diagram.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables giving optimized Cartesian coordinates, numbers of imaginary frequencies, and total energies of various reactants, products, reaction intermediates, and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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