

Observation of Borirene from Crossed Beam Reaction of Boron Atoms with Ethylene

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The small-ring Hückel 2π aromatic compound borirene, $(\text{CH})_2\text{BH}$, has received considerable attention since Volpin et al.¹ suggested that trivalent boron could replace a carbon atom of the isoelectronic cyclopropenyl cation C_3H_3^+ . Ab initio studies of borirene and its derivatives demonstrated the aromatic character of the molecule, which was found to have about 70% of the resonance energy of cyclopropenyl cation and was predicted to be thermodynamically stable.² Isolation of borirene, however, eluded chemists for a long time, and only substituted borirenes were prepared in the laboratory.³ More recently, matrix isolation spectroscopy allowed identification of the borirene molecule formed from reaction of laser ablated boron with ethylene;⁴ the experimental observation of the aliphatic isomers as additional reaction products in the matrix study⁵ stimulated theoretical calculations on the structures and energetics of singlet $\text{C}_2\text{H}_3\text{B}$ species and on the possible reaction pathways.^{5,6} The most stable isomer of gross formula $\text{C}_2\text{H}_3\text{B}$ was found to be borirene (whose aromatic character was confirmed) followed by ethynylborane ($\text{H}_2\text{-BCCH}$) and borallene (H_2CCBH) which are 27 and 102 kJ mol^{-1} , respectively, higher in energy.⁶ The two other possible isomers, $\text{C}_2\text{H}_3\text{B}$ and H_2CBCH , were found to be much less stable.⁶ Andrews et al. suggested the reaction pathways be B addition to the double C–C bond or B insertion into one of the C–H bond;^{4,5} however, the effect of matrix trapping, the poorly defined energy and the unknown composition of the laser-ablated boron reagent do not allow a definite assignment of the reaction mechanism.

Investigation at the molecular level, in a collision-free environment where it is possible to observe the consequences of a single reactive event, can provide a direct insight into the reaction mechanism.^{7,8} Surprisingly, experimental investigation of B atom reactions at the microscopic level has practically eluded the array

of the elaborate experimental techniques devised in the field of reaction dynamics, although such techniques have been successfully used to investigate the reaction dynamics of light, second-row atoms (Li, C, N, O, and F).⁷ We recall that, among those techniques, the crossed molecular beam (CMB) method with mass spectrometric detection turned out to be particularly suitable for investigating reactions giving polyatomic products which are not a priori predictable and whose spectroscopic properties are unknown.^{7,8} The application of such a technique has one stringent prerequisite, that is it must be possible to produce a beam of the unstable (atomic or radical) species of sufficient intensity to carry out angular and velocity distribution measurements of the reaction products.⁸ In our laboratory, we have recently succeeded in generating a pulsed beam of boron atoms by laser ablation of a boron rod⁹ and undertaken a systematic investigation of $\text{B}(\text{P})$ reactions with simple unsaturated hydrocarbons of potential practical interest. The aim is also to gain an insight into the chemical behavior of this atomic species which is still unexplored.

In this contribution, we report the first account on the dynamics of a ground-state $\text{B}(\text{P})$ reaction, namely that with ethylene. By using the CMB technique with mass spectrometric detection and combining our results with electronic structure calculations, our study gives a clear evidence of formation of borirene as primary reaction products under collision free conditions.

We have performed a first scattering experiment at a collision energy, E_c , of 17.6 kJ mol^{-1} using the 35" universal CMB apparatus.¹⁰ Two well-collimated, supersonic beams of the reagents are crossed at 90° in a scattering chamber maintained in the 10^{-7} -mbar range. The reaction products are detected by a rotatable electron impact quadrupole mass spectrometer, contained in an ultrahigh-vacuum ($<8 \times 10^{-13}$ mbar) chamber. Product velocity distributions are obtained using the time-of-flight (TOF) technique at different laboratory scattering angles and for different mass-to-charge ratios (m/e) of the ionized products. Characterization on axis of the pulsed boron beam (obtained by seeding the ablated boron in neat helium) shows that no boron clusters were present. A chopper wheel located after the ablation zone and the skimmer of the primary source selected a slice of the boron beam with a peak velocity of $1611 \pm 15 \text{ m s}^{-1}$ and speed ratio of 8.7 ± 0.2 . The second pulsed beam of ethylene was obtained by expanding 500 Torr of pure C_2H_4 ; peak velocity and speed ratio were $895 \pm 15 \text{ m s}^{-1}$ and 13.0 ± 0.5 , respectively.

Reaction products were detected at $m/e = 38, 37, 36, 35$, and 34 corresponding to the ions $\text{C}_2\text{H}_3^{11}\text{B}^+$, $\text{C}_2\text{H}_2^{11}\text{B}^+/\text{C}_2\text{H}_3^{10}\text{B}^+$, $\text{C}_2\text{H}^{11}\text{B}^+/\text{C}_2\text{H}_2^{10}\text{B}^+$, $\text{C}_2^{11}\text{B}^+/\text{C}_2\text{H}^{10}\text{B}^+$, and $\text{C}_2^{10}\text{B}^+$, respectively. The laboratory distributions of the different ions were found to be superimposable, which unambiguously indicates⁸ that the only detected product is $\text{C}_2\text{H}_3\text{B}$ and that it partly fragments to daughter ions in the electron impact ionizer. No radiative association to $\text{C}_2\text{H}_4\text{B}$ was detected because under single collision conditions, differently from the case of matrix experiments, the initially formed adduct fragments due to its high energy content. Because of the best signal-to-noise ratio, all the final measurements were carried out at $m/e = 37$; the product laboratory angular distribution is shown in Figure 1 (top). Quantitative information on the reaction dynamics is obtained by moving from the lab coordinate system to the CM one and analyzing the product angular, $T(\theta)$, and translational energy, $P(E_T)$, distributions into which the CM product flux can be factorized.⁷ The solid line superimposed on the experimental results in Figure 1 is the calculated curve when using the best-fit CM functions. A convenient way to summarize the dynamical features of the reactive event is to report the CM product flux contour map, where the intensity is given as a function of product CM velocity, u , and scattering angle, θ (Figure 2). The shape of our CM angular distribution is isotropic, that is with the same intensity in the whole angular range, as well visible

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(10) We rather find an intermediate where the B atom attacks only one C atom via a barrier of 10–20 kJ mol^{-1} to form a $\text{BCH}_2\text{-CH}_2$ radical. The most favorable reaction channel of the latter is subsequent ring closure (barrier $\sim 2 \text{ kJ mol}^{-1}$) to borirane.

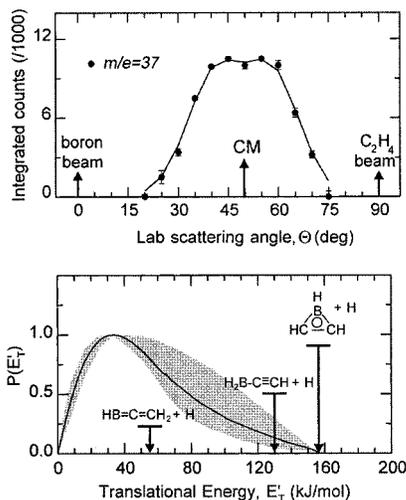


Figure 1. (Top) The C_2H_3B product laboratory angular distribution (detected at $m/e = 37$) from the reaction $B(^2P) + C_2H_4(X^1A_g)$ at a relative collision energy $E_c = 17.6 \text{ kJ mol}^{-1}$. The solid line represents the angular distribution obtained from the best-fit CM angular and translational energy distributions; (Bottom) CM product translational energy distribution. The arrows delimit the maximum energy reachable by the three different isomers corresponding to the general formula C_2H_3B .

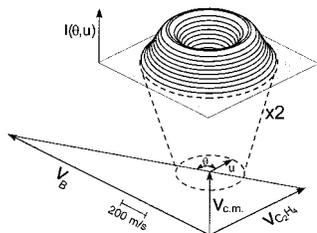


Figure 2. Velocity vector ("Newton") diagram showing the kinematics of the reactive experiment. A three-dimensional perspective of the CM product flux is given as a function of product CM speed, u , and scattering angle, θ . The dashed circle delimits the maximum CM speed achievable by borirene molecule when assuming that all the available energy is released as product translational energy.

in the contour map; this is indicative of the formation of a bound C_2H_4B intermediate during the reaction. The best-fit product translational energy distribution $P(E_T)$ peaks at about 34 kJ mol^{-1} and is characterized by a tail which extends up to 158 kJ mol^{-1} (see Figure 1, bottom). In addition, our experimental results clearly indicate that product(s) of general formula C_2H_3B is (are) formed through the B versus H exchange channel.

To conclusively address the questions: *which is the dominant reaction pathway?*, we can combine our experimental findings with previous⁶ and new electronic structure calculations of the BC_2H_4 potential energy surface; the possible reaction channel together with the computed relevant minima and transition states along the pathway leading to borirene is shown in Figure 3. In principle, $B(^2P)$ can either add to the π bond of the C_2H_4 molecule or insert into one of the C–H bonds leading to the bound intermediates borirane radical, $(CH_2)_2B$, and vinylborane radical, CH_2CHBH , respectively. Our electronic structure calculations unveil that $B(^2P)$ adds indeed without entrance barrier to the ethylene molecule, thus forming the borirane radical, $(CH_2)_2B$, which is stabilized by 217 kJ mol^{-1} with respect to the reactants (B3LYP/cc-pVDZ level; zero-point energy corrected). The borirane radical does not correlate with the ground state of the reactants. However, there is a π -complex correlating with the reactants. In C_s symmetry, this will give $^2A'$ state which would have an avoided crossing with the borirane radical. This radical undergoes then a H atom shift to form the rearranged borirane radical, $CH(BH)CH_2$. Our result correlates strongly with Andrews studies as borirane is the major radical observed in the matrix

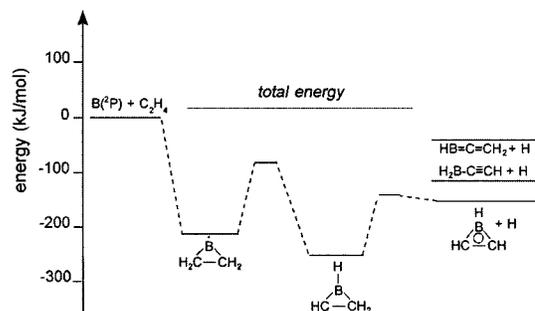


Figure 3. Schematic energy level and correlation diagram for the reaction $B(^2P) + C_2H_4(X^1A_g)$.

experiment as well.⁵ A hydrogen atom elimination from the gas-phase $CH(BH)CH_2$ complex leads finally to borirene formation.

The extent of the translational energy release, determined by the shape of $P(E_T)$, gives us a useful criterion through the energy conservation rule^{7,8} to support our conclusions. The value of the heat of reaction, $\Delta_r H^\circ$, indeed, can be derived from the falloff of the $P(E_T)$. The best-fit of the experimental data is achieved when using the function reported in Figure 1 where the tail extends up to 158 kJ mol^{-1} . This range of energy is consistent with the formation of the borirene molecule. Moreover, the total angular momentum is conserved during the reactive collisions and therefore, since the departing H atom is light compared to the borirene molecule, about 70–85% of the initial angular momentum has to be channeled into rotational excitation of products, implying that part of the available energy is converted into internal excitation of the molecular moiety. This is well documented by the isotropic angular part of the flux contour map since a peaking of the poles at 0° and 180° is clearly not observed.

Based solely on the energetics as calculated at the CCSD(T) level⁶ also the singlet closed shell molecules H_2BCCH and $HBCCH_2$ could be formed as minor reaction products. However, the only route to form these species is via H atom elimination from the allene-like intermediate H_2BCCH_2 , which in turn can be derived from the vinylborane radical, CH_2CHBH , through H migration. However, our ab initio calculations do not locate a transition state for an insertion of $B(^2P)$ into an ethylenic C–H bond.¹⁴

It is also instructive to compare our findings to those for similar systems $X + C_2H_4$. Interestingly, in all cases the interaction of open-shell electrophilic atomic species with the π electrons of ethylene was found to be the dominant approach. A survey of these systems reveals that the most similar case to the title reaction is that of $N(^2D) + C_2H_4$, also recently studied in crossed beam experiments.^{11a} The electronically excited nitrogen atoms can, indeed, add to the π bond of ethylene (forming a cyclic intermediate analogous to the borirane radical) or insert into one of the C–H bonds; the addition pathway was found to be the only active for energies lower than 50 kJ mol^{-1} because of a high energy barrier for direct insertion of $N(^2D)$ into the C–H bond. Interestingly, RRKM simulations show that the formation of cyclic product *2H*-azirine following an H emission from the initial addition intermediate is by far the main reaction pathway.

In conclusion, our study gives a first insight into the mechanism of a reaction of atomic boron with a simple hydrocarbon ethylene to form a neutral heterocyclic 2π aromatic system in the gas phase, that is, the elusive borirene molecule. This is the first time borirene has been detected in the gas phase under well-defined experimental conditions.

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