Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 450 (2008) 178–185
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

A reinvestigation of the gas phase reaction of boron atoms, $^{11}B(^2P_j)/^{10}B(^2P_j)$ with acetylene, $C_2H_2(X^1\Sigma_g^+)$

Fangtong Zhang [a,*], Xibin Gu [a], Ralf I. Kaiser [a,*], Holger Bettinger [b,*]

[a] Department of Chemistry, University of Hawai'i, Honolulu, HI 96822, USA
[b] Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

Received 12 August 2007; in final form 18 October 2007
Available online 25 October 2007

Abstract

The reaction dynamics of ground state boron atoms, $B(^2P_j)$, with acetylene, was reinvestigated and combined with novel electronic structure calculations. Our study suggests that the boron atom adds to the carbon–carbon triple bond of the acetylene molecule to yield initially a cyclic intermediate undergoing two successive hydrogen atom migrations to form ultimately an intermediate **i3**. The latter was found to decompose predominantly to the c-$BC_2H(X^2A')$ isomer plus atomic hydrogen via a tight exit transition state. To a minor amount, an isomerization of **i3**–**i4** prior to a hydrogen atom ejection forming the linear structure, $HBCC(X^1\Sigma^+)$, has to be taken into account. Since the c-$BC_2H(X^2A')$ and $HBCC(X^1\Sigma^+)$ isomers are separated by an isomerization barrier to ring closure of only 3 kJ mol^{-1}, internally excited $HBCC(X^1\Sigma^+)$ products can isomerize to the c-$BC_2H(X^2A')$ structure and vice versa.

1. Introduction

In recent years, boron–carbon clusters and their partially hydrogenated counterparts have received considerable attention both theoretically [1] and experimentally [2–7]. This is due to their importance in semi conductor processes [8,9] and as additives to rocket-propellants [10]. In chemical vapor deposition (CVD) processes involving diborane, hydrogen, and simple hydrocarbons like methane, boron often prevails as a transient reactant [11]; from the industrial viewpoint, these processes are important to manufacture boron-doped diamond films (p-type semiconductors, unconventional superconductor, UV Schottky photodiodes) and boron-doped hydrogenated amorphous carbon films via surface-wave mode microwave plasma CVD and their potential applications to photovoltaic cells [12]. Since atomic boron, $B(^2P_j)$, is isoelectronic with singly ionized carbon atoms, an understanding of elementary boron atom reactions can also assist to understand the chemistry in weakly ionized hydrocarbon plasmas. Here, $C^+(^2P_j)$ presents in important reactant and can contribute, for instance, to the formation of polycyclic aromatic hydrocarbons (PAHs) and their cationic counterparts [13].

In this context, it is important to note that an investigation of the reaction of ground state boron atoms, ^{11}B and ^{10}B, with acetylene has attracted substantial interest. These reactions access experimentally the BC_2H_2, BC_2H, and BC_2 potential energy surfaces (PES) of some of the smallest (hydrogenated) boron–carbon clusters. Small clusters like BC, BC_2 and B_2C were first observed in the early 1960s via mass spectrometry in the vapor phase over solid boron carbide heated to about 2300 K [14]. Later on, these molecules were successfully trapped in solid argon or neon matrices and characterized by electron spin resonance spectroscopy (ESR) [2]. The results suggested the at least one BC_2 isomer had a linear $BCC(X^2\Sigma^+)$ structure. As technology advanced, in 1990s, Martin et al. reinvestigated this system utilizing pulse laser ablation of boron–carbon pellets coupled with matrix isolation spectroscopy [15]. This study concluded that BC_2 was a cyclic molecule with a strong, symmetric BC_2 stretching frequency near 1200 cm^{-1}. Knight et al. confirmed that the ground state

* Corresponding authors. Fax: +1 808 956 5908.
E-mail addresses: fangtong@hawaii.edu (F. Zhang), ralfk@hawaii.edu (R.I. Kaiser), Holger.Bettinger@ruhr-uni-bochum.de (H. Bettinger).

0009-2614/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2007.10.067

of BC_2 in neon, argon, and krypton matrices is in fact the nonlinear symmetric structure with an X^2A_1 electronic ground state,[4] about 26 kJ mol^{-1} below the linear BCC($X^2\Sigma^+$) isomer [5].

The local minima of the BC_2H potential energy surface were studied first via low temperature spectroscopy via reaction of laser ablated boron atoms with acetylene molecules [16]. Besides the BC_2H_2 adducts, Andrews et al. identified two linear BC_2H isomers, i.e. HCCB($X^1\Sigma^+$) and HBCC ($X^1\Sigma^+$). However, the reaction mechanisms to form these structures could not be resolved explicitly. In 2001, Balucani et al. carried out the gas phase reaction of ground state boron atoms, B (^2P_j), with acetylene (C_2H_2($X^1\Sigma_g^+$)) utilizing the crossed molecular beams approach [17]. In this preliminary study, the authors found that the atomic boron versus atomic hydrogen exchange channel was open. The reaction dynamics were suggested to be indirect, proceed via addition of the boron atom to the carbon–carbon triple bond and form – after successive isomerization – the linear HBCC($X^1\Sigma^+$) isomer. In a complementary study, Geppert et al. [18] investigated in both kinetic and dynamic experiments the reaction of boron atoms with acetylene and D_2-acetylene. The authors indicated that both sets of results were best described by the presence of a very weak barrier in the entrance channel of the PES (0.18 kJ mol^{-1}). However, this investigation could not shed light on the nature of the BC_2H isomer(s) formed.

However, various aspects of this reaction have remained unanswered so far. First, due to the enhanced sensitivity and hence increasing signal-to-noise of the present crossed molecular beam experimental setup, we intent to investigate if only the atomic hydrogen or also the molecular hydrogen elimination channel is open. Secondly, we attempt to extract to what extent a hitherto neglected cyclic BC_2H isomer is involved in the chemical dynamics; recall that in the related reaction of ground state boron atoms with acetylene, both the linear and cyclic C_3H isomers were synthesized [17,19]. This study is combined with new, high level electronic structure calculations which can provide reaction energies within chemical accuracy (±5 kJ mol^{-1}). This will also allow us to reinvestigate the experimentally obtained reaction energy to form BC_2H isomer(s) within much lower error bars than studied previously to be compared with the new theoretical data.

2. Experimental setup, data analysis, and theoretical methods

The elementary reaction of ground state boron atoms, B(^2P_j), with acetylene, C_2 H_2($X^1\Sigma_g^+$) was studied in a universal crossed molecular beams machine under the single collision conditions. Briefly, a pulsed boron atom beam was generated in the primary source chamber by laser ablation of a boron rod at 266 nm (30 Hz) and seeded in neat helium carrier gas (99.9999%, Airgas; 4 atm) released by a Proch–Trickl pulsed valve. As monitored by the mass spectrometric detector, the ablation beam contains both ^{11}B and ^{10}B species in their nature abundances. After passing a skimmer, a four-slot chopper wheel selected a part out of the boron beam at a peak velocity v_p of 2070 ± 10 m s^{-1}; a speed ratio of 3.5 ± 0.2 was obtained. This part crossed a pulsed acetylene beam (99.99% after removal of acetone via zeolite traps and acetone-dry ice bath; 550 torr) released by a second pulsed valve perpendicularly in the interaction region. The segment of the acetylene beam was characterized by a peak velocity of 950 ± 20 m s^{-1} and a speed ratio of S = 16.0 ± 1.0. For the $^{11}B/C_2H_2$ and $^{10}B/C_2H_2$ systems, collision energies of 20.1 ± 0.2 kJ mol^{-1} and 18.7 ± 0.2 kJ mol^{-1}, respectively, were obtained. The reactively scattered species were monitored using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the molecules at 90 eV. This detector could be rotated within the plane defined by the primary and the secondary reactant beams to allow taking angular resolved TOF spectra at specific mass-to-charge (m/z) ratios. At each angle,

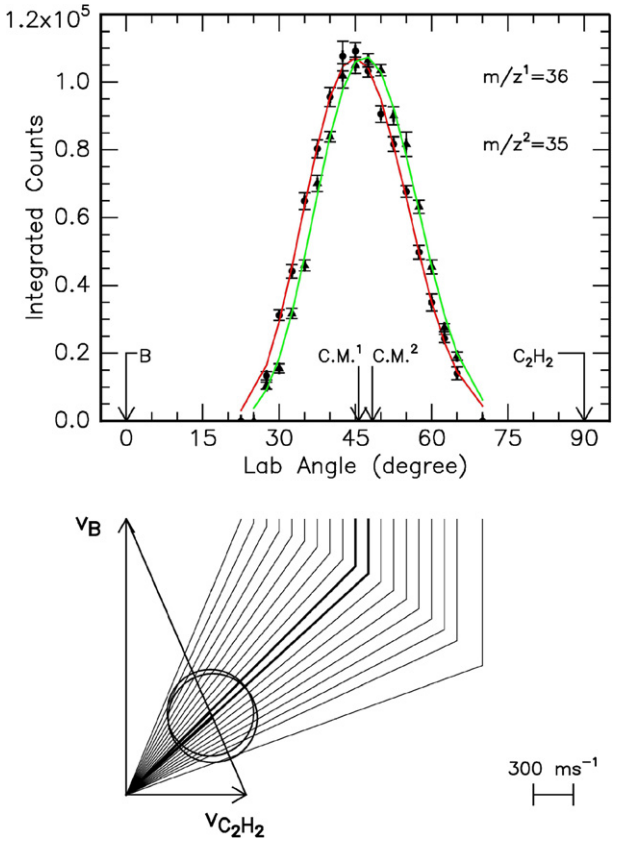

Fig. 1. Lower: Newton diagram for the $^{11}B/C_2H_2$ and $^{10}B/C_2H_2$ systems investigated. The circles show the maximum center-of-mass recoil velocity of the cyclic $^{11}BC_2H/^{10}BC_2H$ isomers assuming that no energy channels into the internal degrees of freedom. Upper: Laboratory angular distribution of the $^{11}BC_2H/^{10}BC_2H$ products at $m/z = 36$ (red) and 35 (green) respectively. Circles/triangles and 1σ error bars indicate experimental data, the solid red/green lines indicate the calculated distribution. The center-of-mass angles are indicated by C.M. The solid lines originating in the Newton diagram point to distinct laboratory angles whose times-of-flight are shown in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).