J. Phys. Chem. A **2004,** *108,* 6183−6185

Experimental Kinetics Study of the Reaction of Boron Atoms, $B(^2P_J)$, with Ethylene at Very Low Temperatures (23−295 K)

André Canosa,*,[†] Sébastien D. Le Picard,[†] and Wolf D. Geppert[‡]

Laboratoire de Physique des Atomes, Lasers, Molécules et Surfaces, UMR 6627 CNRS−Université de Rennes 1, Campus de Beaulieu, 35 042 Rennes Cedex, France, and Department of Molecular Physics, University of Stockholm, Alba Nova, Roslagstullbacken 21, Stockholm S-10691, Sweden

Received: March 22, 2004; In Final Form: May 17, 2004

The kinetics of the reaction $B(^2P_J) + C_2H_4$ has been investigated between 23 and 295 K in a continuous flow CRESU (cinétique de réaction en écoulement supersonique uniforme) apparatus using pulsed laser photolysis of trimethyl borate, $B(OCH_3)_3$, to generate $B(^2P_J)$ atoms and laser-induced fluorescence to observe the kinetic decay of the boron atoms and hence determine the rate coefficients. The thermal rate constant temperature dependency is well described by the following expression: $k(T) = (1.86 \pm 0.40) \times 10^{-10} (T/300)^{-(0.70\pm0.30)} \times \exp(-(26 \pm 14)/T)$ cm^3 molecule^{-1} s^{-1} indicating the absence of any significant activation barrier in the entrance channel of the potential energy surface of the title reaction.

Introduction

Boron chemistry has received special attention because of its interesting position between metal and nonmetal atoms. Reactions with boron atoms have also been studied for their interest in the fields of combustion,[1] semiconductor manufacturing,[2] and organoboron synthesis.[3] In the past few years, the mechanisms of reactions involving boron ground-state atoms, $B(^2P_J)$, and hydrocarbon molecules have been investigated both theoretically and experimentally.[4−10] Among those, the reaction between boron atoms and ethylene presents a particular interest because it was shown that this reaction could lead to the formation of borirene,[5,7] $(CH)_2BH$, the smallest aromatic molecule well-known in organic synthesis.[11,12] The mechanism most recently suggested for this reaction pathway, deduced from the observation of borirene in a crossed beam experiment,[7] is the addition of boron atoms to the ethylene molecule without entrance barrier, forming the borirane radical, $(CH_2)_2B$, followed by the shift of an H atom before its elimination.

Experimental reaction kinetics studies at very low temperature ($\ll$300 K) provide a way to detect the presence of any small barrier in the entrance channel of the potential energy surface. In this paper we present the first experimental determination of the rate coefficients of the title reaction over the temperature range of 23−295 K. Experiments were performed using the CRESU (cinétique de réaction en écoulement supersonique uniforme) apparatus of Rennes, in conjunction with the PLP−LIF (pulsed laser photolysis−laser-induced fluorescence) technique for the production and detection of ground-state boron atoms.

Experimental Section

The CRESU method, as applied to neutral−neutral reactions, has already been described in detail elsewhere.[10,13]

Briefly, low temperatures are achieved by the isentropic expansion of a gas mixture through a Laval nozzle. A supersonic flow is generated in which the temperature, density, and velocity are uniform along the flow. This temperature is a true thermodynamic temperature as the density of the flow (from 10^{16} to 10^{18} molecules cm^{-3}) is high enough to ensure thermal equilibrium by collisions. The nozzle is mounted on a moveable reservoir kept at room temperature, into which the carrier gas, the reagent gas (ethylene), and the precursor of the boron atoms (trimethyl borate, $B(OCH_3)_3$, hereafter referred to as TMB) are introduced, after passing through mass flow controllers (Tylan) and being mixed together prior to expansion.

Boron atoms were produced in the supersonic flow by multiphoton photolysis of TMB using the fourth harmonic (266 nm) of a pulsed YAG laser beam (Spectra Physics, GCR 190, 10 Hz, 50 mJ) propagated along the flow and mildly focused at the nozzle exit by means of a converging lens (37 cm focal length) located inside the reservoir. A tuneable pulsed laser (Spectra Physics, MOPO 730 with frequency-doubling option, 10 Hz, ~10 μJ) propagated perpendicularly to the flow and excited either the $2s^22p(^2P_{1/2})-2s^23s(^2S)$ or the $2s^22p(^2P_{3/2})-2s^23s(^2S)$ transition of atomic boron at 249.677 and 249.772 nm, respectively. Because of the small spin−orbit splitting in $B(^2P_J)$, the $B(^2P_{3/2})$ state lying only 15.3 cm^{-1} above the ground-state $B(^2P_{1/2})$, collisional relaxation of the nascent spin−orbit distribution was observed to be very fast (<1 μs) in our experimental conditions. The resonant fluorescence signal was collected onto the photocathode of a UV-sensitive photomultiplier tube after passing through a narrow band interference filter (centered at 250 nm).

The time delay between the two laser pulses was set equal to the time necessary for the boron atoms formed at the focal point to reach the detection zone. The LIF signal from the $B(^2P_J)$ atoms was measured and averaged over 200 laser shots for different ethylene flow rates. As shown in Figure 1, its variation with ethylene concentration was well fitted using a single-exponential function $y - y_0 = a \exp(-\beta[C_2H_4])$, where β (in cm^3 molecule^{-1} units) can be identified as the product of the bimolecular rate coefficient of the reaction, k, and the time delay, Δt, when pseudo-first-order conditions are met. Such a set of measurements was then repeated for different focal point

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* Corresponding author. E-mail: Andre.canosa@univ-rennes1.fr. Phone: +33 (0)223 23 69 96. Fax: +33 (0)223 23 67 86.

[†] Université de Rennes 1.

[‡] University of Stockholm.

10.1021/jp048732r CCC: $27.50

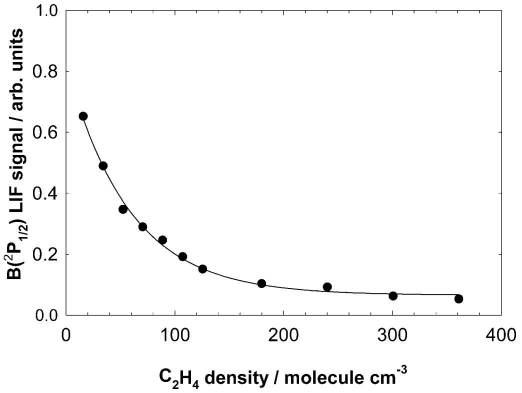

Figure 1. Boron atoms, $B(^2P_{1/2})$, fluorescence signal as a function of ethylene density at 24 K for a time delay between the two lasers set to 50 μs.

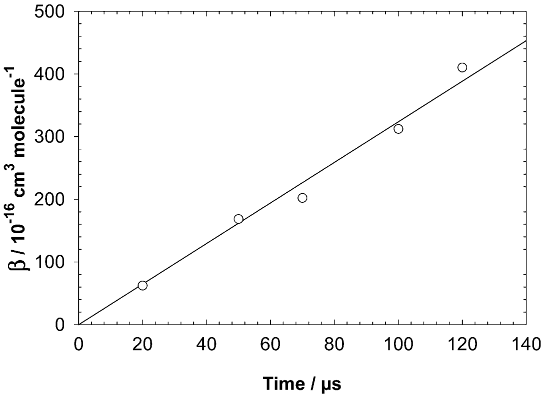

Figure 2. Plot of the pseudo-first-order coefficients, β, as a function of the time delay for $B(^2P_J) + C_2H_4$ at 24 K.

positions by moving the Laval nozzle so that several β were obtained and plotted as a function of the time delay. This is illustrated in Figure 2 where data are well fitted using a straight line, crossing both axes at the origin. The slope of this line gave the bimolecular rate coefficient k (in cm^3 molecule^{-1} s^{-1} units) for the conditions of temperature and pressure for the particular Laval nozzle used.

Results and Discussion

The experimental results are summarized in Table 1 and the temperature dependence of the rate coefficients for the reaction of $B(^2P_J)$ with molecular ethylene is plotted in Figure 3 on a log−log scale. Only statistical errors are quoted. Some systematic errors due to flow control inaccuracies or inaccuracies in the determination of the buffer gas total density should also be taken into account; the additional error, however, does not exceed 10%. It is worth noting that we checked that the rate coefficient measured was pressure independent using a nozzle working in He at 23 K at much lower density (4.7×10^{16} cm^{-3}) than the nozzle working in He at 24 K (18.3×10^{16} cm^{-3}): no significant difference was found for the rate coefficients obtained. Furthermore, the rate constant measured at 97 K in argon is consistent with the rate coefficients obtained using helium as a buffer gas at other temperatures as can be seen in Figure 3. This emphasizes, therefore, that three-body association is not a factor for this reaction.

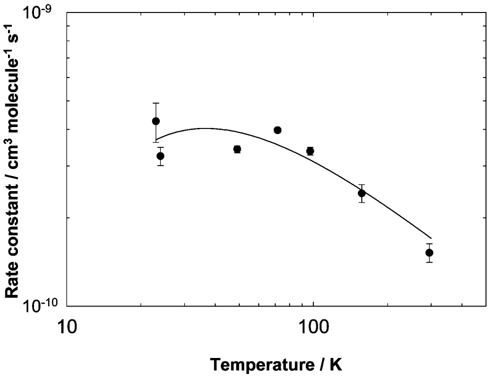

Figure 3. Rate constants for the reaction of $B(^2P_J) + C_2H_4$ as a function of temperature plotted on a log−log scale. The solid line shows the result of a fit of the CRESU data yielding: $k(T) = (1.86 \pm 0.40) \times 10^{-10} (T/300)^{-(0.70\pm0.30)} \exp(-(26 \pm 14)/T)$ cm^3 molecule^{-1} s^{-1}.

The experimental values of the rate coefficient as a function of temperature can be fitted by the following analytical expression: $k(T) = (1.86 \pm 0.40) \times 10^{-10} (T/300)^{-(0.70\pm0.30)} \times \exp(-(26 \pm 14)/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range of 23−295 K, as illustrated in Figure 3. The rate coefficient seems to exhibit a maximum value at ca. 50 K. The presence of a maximum in the T-dependence of the rate coefficient has already been observed in different experiments studied at very low temperatures in the CRESU apparatus.[14,15] For some of them,[15] the adiabatic capture theory used to reproduce the temperature dependence of the reaction showed that this maximum could be explained by the difference of reactivity of the spin−orbit states of the atom involved. Such differences of reactivity have also been observed in the crossed molecular beam experiment of Bordeaux at very low kinetic energies.[16] Recently, however, we studied the reaction between boron atoms and acetylene using conjointly the CRESU apparatus of Rennes and the crossed molecular beam experiment of Bordeaux.[10] A maximum in the temperature dependence was also observed at ca. 50 K and was explained by the presence of a very weak barrier (0.18 kJ/mol) in the entrance channel of the potential energy surface. The height of this barrier was estimated from the translational energy dependence of the integral cross sections (excitation function) obtained in the crossed molecular beam experiment. It cannot be deduced from our CRESU experiments, however, whether the presence of the maximum in the temperature dependence of the rate constant is due to a difference of reactivity of the two spin−orbit states

TABLE 1: Experimental Conditions of the CRESU Experiments

T/K	buffer gas	total density/ $\times 10^{16}$ cm^{-3}	[C_2H_4]/ $\times 10^{13}$ cm^{-3}	Δt range/ μs	rate constant/ ($\times 10^{-10}$ cm^3 molecule^{-1} s^{-1})
23	He	4.7	0.7−52	20−50	4.26 ± 0.65[a]
24	He	18.3	3−84	20−100	3.24 ± 0.23
49	He	10.4	2−73	35−95	3.42 ± 0.09
72	He	6.0	0.4−23	50−90	3.97 ± 0.07
97	Ar	15.5	2−60	25−125	3.37 ± 0.10
158	He	13.0	0.6−81	10−65	2.42 ± 0.17
295	He	11.5	8−237	15−50	1.52 ± 0.11

[a] Errors quoted are ± $t\sigma$ errors where t is the value of the Student's t-distribution for the 95% point.

of boron atoms or to the presence of a very weak barrier ($\ll$1 kJ/mol) in the entrance channel of the potential energy surface. Because of the very fast (<1 μs) collisional relaxation of the spin−orbit states (B($^2P_{1/2}$) and B($^2P_{3/2}$)) in our experimental conditions ($n \sim 10^{16}-10^{17}$ molecule cm^{-3}), indeed, 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 coefficients.

To our knowledge there is no other kinetic study of the title reaction in the gas phase, even at room temperature. Kaiser and co-workers, however, recently studied this reaction using a crossed beam apparatus at a collision energy of 17.6 kJ/mol[7] and observed the formation of product(s) of the general formula C_2H_3B. Theoretical calculations[6,7] have shown that the B(^{2}P) atom could add to the π bond of the C_2H_4 molecule without an entrance barrier to form the borirane radical, (c-BC_2H_4). Energetically, three molecules can be formed from borirane radical: ethynylborane (H_2BCCH), bollarene (H_2CCBH), and borirene (c-HBC_2H_2), the most exothermic mechanism being the latter with 33−36 kJ/mol.[17] However, no transition state for an insertion of B(^2P_J) into an ethylenic C−H bond, necessary to form ethynylborane or bollarene, was found by Balucani et al. using ab initio calculations.[7] Borirene is likely to be, therefore, the major product of the title reaction.

Acknowledgment. The Rennes group acknowledges support from the “Programme National Physique et Chimie du Milieu Interstellaire”. The Rennes group and W.D.G. are grateful for support of their collaboration via the provision by the EU of a TMR Research Network Grant, Contract FMRX-CT97-0132 (DG12-MIHT), for research on astrophysical chemistry.

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