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Evidence for Higher Reactivity of B_2. Theoretical Studies of Insertions of B_2 and B into Methane and Water

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Abstract: The insertions of B_2 and B into methane and water have been chosen as models to study the reactivities of atom dimers vs bare atoms. At our highest theoretical level (B3LYP/6-311++G(3df,2p)//B3LYP/6-311++G-(2d,p)), the activation energies for B_2 insertions into methane and water are predicted to be 4.1 and −6.7 kcal/mol, respectively, while the values increase to 16.2 and 0.0 kcal/mol for insertions of B into two substrates, which shows directly that B_2 have a higher reactivity than B in inserting into the two substrates. In addition, two new species $CH_3BH(B)$ and HOBH(B) are theoretically predicted.

The reaction of bare atoms/clusters with compounds has been a very active field of research. As an important class of reactions, the insertion of bare atoms into molecules such as CH_4, CH_3-Hal, NH_3, H_2O, C_2H_2, and C_2H_4 has interested scientists for many years.[1−15] However, there has been less attention paid to the insertion of atom dimers/clusters, and there is little knowledge about the reactivities of atom dimers/clusters vs atoms. To our knowledge, although several experimental and theoretical studies[2,11,12] have indirectly shown that some atom dimers/clusters are more reactive than bare atoms, no direct and detailed experimental and theoretical evidence to prove it has been reported. In this study, we choose the insertions of B_2 and B into methane and water as models to study the reactivities of atom dimers vs bare atoms, and show direct theoretical evidence for the higher reactivity of B_2 compared to the single B atom.

The hybrid B3LYP DFT method[16,17] was applied to optimize fully structures of the stationary points under investigation with basis sets,[18] 6-31G(d), 6-311++G(d, p), and 6-311++G(2d,p). The B3LYP/6-31G(d) frequency calculations were employed to characterize the stationary points, and to estimate zero point energy (scaled by a factor of 0.9804[19]) contributions to the relative energies. Finally, the energetic results were refined by performing single point B3LYP/6-311++G(3df,2p) calculations at the B3LYP/6-311++G(2d,p) geometries. In the following the highest level energetic and geometric results are used unless otherwise noted. The spin contaminations in the unrestricted calculations are negligible.

The insertions of B_2 and B into CH_4 and H_2O are predicted to occur according to the following reaction schemes:

$$B_2 + CH_4 \rightarrow TS \rightarrow CH_3BH(B) \tag{1}$$

$$B + CH_4 \rightarrow TS \rightarrow CH_3BH \tag{2}$$

$$B_2 + H_2O \rightarrow B_2{-}OH_2 \rightarrow TS \rightarrow HOBH(B) \tag{3}$$

$$B + H_2O \rightarrow B{-}OH_2 \rightarrow TS \rightarrow HOBH \tag{4}$$

The energetic results are listed in Table 1. It is noted that the relative energy values in columns 6 to 8 are quite close,

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Table 1. Relative Energies[a] (kcal/mol) for the Intermediate Complexes, Transition States, and Products, Together with the B3LYP/6-31G(d) Zero Point Energies (ZPE), and the Imaginary Frequencies (IMG) for the Transition States

		ZPE[b] kcal/mol	IMG, cm^{-1}	6-31G(d)	6-311++G(d,p)	6-311++G(2d,p)	6-311++G(3df,2p)[d]
$B_2 + CH_4$	1a	29.3		0.0 (−89.93405)[c]	0.0 (−89.96125)	0.0 (−89.96319)	0.0 (−89.96574)
TS	1c	28.4	731.7i	7.3	4.6	4.4	4.1
$CH_3B(B)H$	1d	30.4		−74.2	−73.7	−73.9	−74.2
$B + CH_4$	2a	27.8		0.0 (−65.17273)	0.0 (−65.19642)	0.0 (−65.19755)	0.0 (−65.19946)
TS	2c	24.8	850.8i	19.0	16.9	16.6	16.2
CH_3BH	2d	27.4		−62.0	−61.3	−61.7	−62.0(−56.2)[e]
$B_2 + H_2O$	3a	14.5		0.0 (−125.82461)	0.0 (−125.88582)	0.0 (−125.88786)	0.0 (−125.89233)
$B_2 - OH_2$	3b	17.3		−15.4	−13.8	−14.3	−14.8
TS	3c	13.7	1368.9i	−9.3	−5.6	−6.3	−6.7
HOB(B)H	3d	17.2		−104.5	−95.6	−96.8	−97.1
$B + H_2O$	4a	13.0		0.0 (−101.06330)	0.0 (−101.12100)	0.0 (−101.12222)	0.0 (−101.12604)
$B - OH_2$	4b	14.2		−7.3	−5.1	−4.9	−5.1
TS	4c	10.9	1191.1i	−3.3	1.2	0.2	−0.0
HBOH	4d	14.7		−103.1	−94.1	−95.7	−95.9 (−100.0)[f]

[a] Corrected with the B3LYP/6-31G(d) zero point energies (scaled by a factor of 0.9804). [b] Scaled zero point energies. [c] Values in parentheses are the total energies in au. [d] Single point calculations at the B3LYP/6-311++G(2d,p) geometries. [e] From ref 20, $E_{G2}(CH_3BH) = -65.10243$ au, $E_{G2}(B+CH_4) = -65.01292$ au. [f] From ref 4.

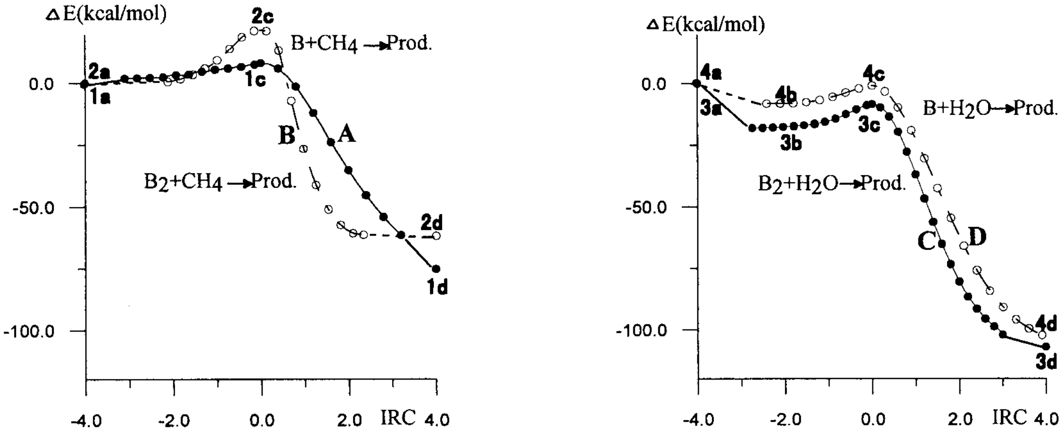

Figure 1. Minimum energy paths for reactions 1−4 at the B3LYP/6-31G(d) level.

and the largest discrepancy with those in column 5 is not more than 4 kcal/mol except for **3d** and **4d**. Reaction 4 is exothermic by 95.7 kcal/mol, in agreement with previous theoretical values of about 100 kcal/mol.[4] The predicted exothermic value of 62.0 kcal/mol for reaction 2 is closer to the G2 value of 56.2 kcal/mol [20] than the CCSD/DZP value of 49.1 kcal/mol.[10] The curves A−D in Figure 1 depict the variations of the energies relative to the respective reactants with the intrinsic reaction coordinates (IRCs) for reactions 1−4, respectively, which shows clearly that the energy barrier for B_2 insertion into either CH_4 or H_2O is lower than that for the corresponding B atom insertion. The activation energies for B_2 insertions into CH_4 and H_2O are predicted to be 4.1 and −6.7 kcal/mol, respectively, while the values increase to 16.2 and 0.0 kcal/mol for the B atom. *The energetic results indicate that boron dimer has a higher reactivity compared to a single boron atom in inserting into methane and water.* To this point, it is helpful to mention the previous studies of the reactions of carbon and dicarbon with methane and water. Experimentally, under matrix conditions, Klabunde and co-workers[12] have shown that the ground-state C(^{3}P) carbon does not react with methane and water, while C_2 reacts with the two substrates. At the MP3/6-31G(d,p)//HF/3-21G + ZPE level, McKee et al.[13] predicted the activation energy for insertion of C(^{3}P) into methane to be 38.1 kcal/mol, and Sakai et al.[14] reported a value of 30.6 kcal/mol at the MP4/6-31G(d,p)//HF/6-31G(d) level, which implies that the reaction takes place very difficultly, in agreement with the experimental results.[12] The barrier height for insertion of C_2 ($^1\Sigma_g^+$) into methane was calculated to be 18.3 kcal/mol[15] at the MP2(full)/6-31G(d) level, but the value lowered significantly to −0.4 kcal/mol[15] at the G2 level. The energetic results imply that the insertion of C_2 into methane occurs favorably, which seems to contradict the experimental assumption[12] that it occurs by the hydrogen abstraction process. For the reaction of C_2 with water,

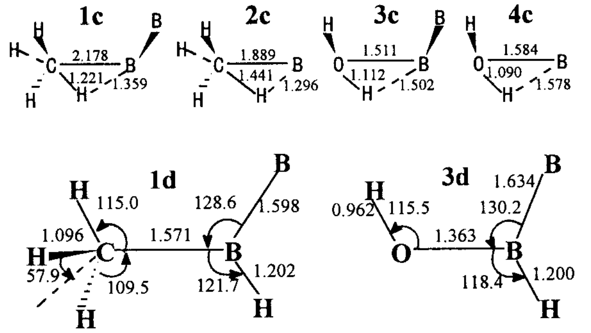

Figure 2. Optimized structures of transition states (**1c**−**4c**) and products (**1d** and **3d**). The values given are the geometric parameters at the B3LYP/6-311++G(2d,p) level. Bond lengths are given in Å and angles in deg.

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Table 2. Calculated (B3LYP/6-31G(d)) Frequencies (cm^{-1}, Scaled by a Factor of 0.9613[19]) and Infrared Intensities (in parentheses, km/mol) for Insertion Products of Reaction 1 to 4

$CH_3B(B)H$	3002 (22), 2956 (14), 2908 (6), 2469 (60), 1443 (4), 1437 (4), 1302 (6), 1111 (64), 974 (6), 832 (11), 766 (5), 711 (0.2), 574 (0.1), 203 (0.8), 120 (2)
CH_3BH	2984 (17), 2930 (10), 2877 (2), 2536 (120), 1431 (7), 1406 (3), 1291 (32), 981 (15), 970 (26), 652 (1), 591 (0.1), 109 (2)
HOB(B)H	3633 (43), 2481 (72), 1269 (318), 1105 (91), 927 (58), 761 (1), 740 (1), 534 (110), 283(3)
HOBH	3610 (73), 2496 (108), 1297 (132), 1079 (97), 853 (72), 734 (60)

although experimentalists[12] found evidence for its occurrence, no conclusions were made about its reaction mechanism. The structures of transition states, together with the most important geometric parameters involved in the insertion processes, are displayed in Figure 2. The four transition states are three-centered ones, which are similar to that for C_2 insertion into methane,[15] but in contrast to the previous proposals,[11b−d] four-centered transition states for the insertion of Mg_2 into R-Hal. In those structures the inserted C−H and O−H bonds are inclined to break, while the other two bonds, B−H and X−B (X = C and O), are inclined to form. It should be pointed out that B_2 is much more stable than Mg_2

Klabunde and co-workers[7] investigated the four reactions, and found that B_2, as well as the B atom, is very efficiently consumed by CH_4 and H_2O. According to our energetic results, reaction 1, 3, and 4 are expected to occur favorably due to the small or negative activation energies, in agreement with the experimental facts.[5,7,8−10] For reaction 2, semiempirical calculations[3] proposed it take place without energy barrier. Our predicted energy barrier (16.2 kcal/mol) for this reaction seems to be slightly larger for its occurrence at low temperature. We suggest that its occurrence under the experimental conditions may be due to the participation of the hyperthermal boron atom from laser ablation (it is possible, see ref 8). Note that the barrier for insertion of Al into CH_4 was predicted to be as high as 49.4 kcal/mol.[6] Sakai and Jordan[4] reported a barrier of 11.9 kcal/mol for reaction 4, which is much larger than our present value (0.0 kcal/mol). We attribute the larger difference to the strong electron correlation effect, which has been found in our previous works,[21,22] as they[4] stated "multireference CI or MCSCF calculations should give a significantly lower transition state".

The new species**, 1d** and **3d**, are predicted to be 74.2 and 97.1 kcal/mol lower in energy than their reactants **1a** and **3a**, respectively, and their structures are displayed in Figure 2. **1d** and **3d** have the structures more similar to $CH_3MgF(Mg)$[11e] that has less total energy compared to CH_3MgMgF.[11a,c,e] Comparing with the product of C_2 insertion into methane,[15] it can be found that, in **1d** and **3d** the onlooking boron is far away from the inserted hydrogen (the distances between the two atoms are 2.302 and 2.354 Å in **1d** and **3d**, respectively), while the onlooking carbon is close to the inserted hydrogen (the distance between the two atoms is 1.268 Å at the MP2(full)/6-31G(d) level). The difference can also be found between **1d** (or **3d**) and $CH_3MgF(Mg)$. Table 2 lists the B3LYP/6-31G(d) vibration frequency values and infrared intensities for **1d** and **3d**, including those for **2d** and **4d**. For **2d**, it is not difficult to find the vibration frequencies corresponding to the FT-IR bands,[7,9,10] and to previous theoretical values.[11] Of particular interest, the frequencies used to characterize the possible identification of **2d** may be presented in **1d.** For example, the frequencies related to the terminal B−H stretching modes of **1d** and **2d** are predicted to be 2469 and 2536 cm^{-1}, respectively, both of which are close to the FT-IR band value[7] of about 2494 cm^{-1}. Thus, we suggest there may be species such as **1d** produced in Klabunde's experiment.[7] It may be recognized also for **3d** and **4d**. Note that there was disagreement in assigning the FT-IR bands for the B + H_2O reaction system.[7,8]

The B_2 and B insertions into CH_4 are different from those into H_2O. For each of reactions 3 and 4, an intermediate complex prior to the transition state is predicted, while for reactions 1 and 2, no species such as **3b** and **4b** can be located. In our previous works, it was found that each of the insertions of CH[21] and SiH[23] into hydrides such as NH_3, H_2O, HF, etc. exists an intermediate complexes prior to the transition state along the insertion paths, and no complexes can be found for the insertions of CH[21] and SiH[24] into methane. Qualitatively, since the orbital structure of the B atom and of the B atom in B_2 is similar to that of the C atom of CH or of the Si atom of SiH, we attribute the formation of intermediate complexes in reactions 3 and 4 to the interaction between lone pair(s) on the oxygen atom of water and the empty p orbitals of the B atom as we did previously.[21,23] Mulliken population showed the OH_2 fragments in **3b** and **4b** have 0.368e and 0.305e positive charges, respectively, which is in agreement with previous proposals for the $B^{\sigma-}$-$OH_2{}^{s+}$ species.[25]

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