Theoretical Study of the Effects of Structure and Substituents on Reactivity in Allylboration

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To clarify the structural factors controlling the reactivity of allylboron derivatives in allylboration, we have carried out a theoretical analysis by applying the ab initio MO method. Electrophilicity of the boron center in several types of allylboron models has been estimated by projecting out the unoccupied reactive orbital that has the maximum amplitude on a boron p-type atomic orbital chosen specifically. Two important factors, the electron-accepting level and vacancy of the orbital of the reaction site, have been included for the purpose of comparing the relative reactivity of those molecules. The theoretically estimated electrophilicity of the boron center is mostly in agreement with experimental observations for allylborons with different chiral auxiliary structures, indicating that electron delocalization from the oxygen of an attacking aldehyde to the boron of an allylboron reagent dominates the reaction. The activation energies of the reaction have been calculated by locating the complex and the transition states on the potential surfaces to compare with the experimental results and the theoretically estimated electrophilicity.

Introduction

Aldehydes react with a variety of allylmetallic compounds to give homoallylic alcohols.[1−13] In particular, the importance of allylboron reagents in acyclic stereoselection was demonstrated in the middle of the 1980's.[14−16] Since then, the research interest in this field of chemistry has been focused on the development of new reagent species that provide high diastereoselectivity.[17−25] As usual, it is difficult to deduce from the experimental results reported by many research groups how reactive a particular reagent is. Meanwhile, Brown and co-workers carried out a systematic investigation to clarify the effects of the solvent, the temperature, the structure of aldehydes, and the structure of the chiral auxiliary in allylborons.[26] As for the effect of the auxiliary, they suggested that the observed variations in the rates of allylboration of the boronate derivatives could be rationalized in terms of the availability of the lone pairs of electrons on the atoms attached to boron. Despite these results, it remains still unclear in some cases to determine how reactive a particular reagent is relative to the other. A clear understanding of the mechanism of the reaction and the factors controlling allylboration is vital for designing new reagents. Thus, we have undertaken a theoretical study to estimate the reactivity of boron in allylboron species.

Results and Discussion

Computational Methods. We examine here cyclic and acyclic allylborons some of which have been investigated in the experimental study by Brown and co-workers and some of which are simplified or hypothetical

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Table 1.   Activation Energies for the Reaction of Allylboron Reagents with Formaldehyde[a]

species	allylboron compounds	formaldehyde	complex	transition state	activation energy[b]
1	−369.069 65	−113.866 33		−482.903 66[c]	
	−370.202 43	−114.183 50	−484.397 28	−484.383 17	8.85[d]
2	−408.109 32	−113.866 33		−521.942 22[c]	
	−409.390 20	−114.183 50	−523.584 83	−523.570 89	8.75[d]
3	−349.225 34	−113.866 33		−463.051 54[c]	
	−350.356 69	−114.183 50	−464.550 98	−464.530 88	12.61[d]
4	−329.380 38	−113.866 33		−443.195 44[c]	
	−330.511 15	−114.183 50	−444.702 70	−444.677 15	16.03[d]
5	−292.174 47	−113.866 33		−406.009 56[c]	
	−293.052 00	−114.183 50	−407.245 21	−407.231 04	8.89[d]
11	−340.192 10	−113.866 33		−454.048 78[c]	
	−341.026 57	−114.183 50	−455.226 05	−455.224 98	0.67[d]

[a] Total energy is given in hartrees. [b] Activation energy is given in kcal/mol. [c] RHF/6-31G*. [d] MP2/6-31G**.

models. To make ab initio MO calculations feasible, we set up simplified reaction models each of which consists of an allylboron reagent molecule and a formaldehyde molecule. The calculations of the transition state were made at the MP2/6-31G** level by using the Gaussian 94 program.[27−30] We attempt, in this study, to connect the reactivity with the electron-accepting ability of those reagents, which is estimated by projecting out the reactive unoccupied orbital centered on the boron atom.

Structures and Energetics. The structure of *B*-allyl-1,3,2-dioxaborolane (**1**) in an isolated state and the structure of the transition state for the reaction of **1** with formaldehyde are illustrated in Figure 1. The reaction is shown to take place via a transition state having a chair form six-membered ring. The B−O and B−C bonds have been calculated to be 1.616 and 1.673 Å, respectively, at the MP2/6-31G** level of the theory, which are seen to be considerably shorter than the Si−O and Si−C bonds, 1.997 and 2.044 Å, respectively, in the reaction of allylsilacyclobutane with formaldehyde.[31] The transition state is more compact in the reaction of boronate.

1

We have examined whether complexes intervene in the course of the reaction.[3,22] The RHF/6-31G** calculations did not show the presence of any complex species. On the other hand, the calculations at the MP2/6-31G** level of theory suggested intervention of some complex species between allylborons and formaldehyde before reaching the transition state. Those complexes are stabilized by 5−7 kcal/mol relative to the starting materials, as shown

Figure 1. Structures of *B*-allyl-1,3,2-dioxaborolane in an isolated state and the transition state for the addition of formaldehyde calculated at the MP2/6-31G** level of theory.

Figure 2. Structure of the complex between *B*-allyl-1,3,2-dioxaborolane and formaldehyde calculated at the MP2/6-31G** level of theory.

in Table 1 for **1**, *B*-allyl-1,3,2-dioxaborinane (**2**), *B*-allyl-1,3,2-oxazaborolidine (**3**), *B*-allyl-1,3,2-diazaborolidine (**4**), and allylboronic acid (**5**). The aldehyde molecule approaches allylborons, directing one of the lone-pair orbitals to the boron atom. But, the B−O distance is pretty large in these complexes, as illustrated in Figure 2 for **1**. According to the MP2/6-31G**−NBO analysis, the amount of the electronic charge shifted from the aldehyde part to the allylboron part is very small, being 0.016 in

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(29) We have carried out a CASSCF (4,4)/6-31G* calculation for the reaction of **1**. The coefficient of the ground-state configuration was found to be 0.97, being very close to 1.
(30) As for the electron correlation effect in the reactions of boron compounds, see, for example, Wang, X.; Li, Y.; Wu, Y.-D.; Paddon-Row: M. N.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 2601.
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1.[32] These results indicate that the two molecules are bound together principally by the Coulombic attraction. The transition state has been located 8−16 kcal/mol above the complex. The order of reactivity estimated from the values of the activation energy is **1** ≈ **2** ≈ **5** > **3** > **4**. However, the reactivity trend has been shown to remain unchanged, even if we disregard the presence of complexes. Complexes may appear in the course of the reaction of allylborons in a nonpolar solvent, but it is difficult to draw a decisive conclusion at this moment.

Brown and collaborators have shown that **1** reacts with benzaldehyde at 25 °C more rapidly than does **2**, with $t_{1/2}$ being 5 min for the former and 40 min for the latter in dichloromethane.[26] They conjectured that boronates having a five-membered cyclic boronate auxiliary should be less sterically hindered relative to those possessing a six-membered cyclic boronate auxiliary. It is seen in Table 1 that the activation energies are very similar in **1** and in **2**. The benzaldehyde reagent has been replaced by a formaldehyde molecule for our computational feasibility, and therefore, the steric factor does not appear in the present calculations.
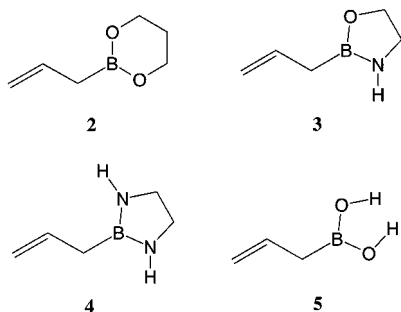
Brown and collaborators have reported that the rates of the reactions of *N*-methyl- and *N*-phenyl-substituted species of **3** with benzaldehyde at 25 °C are approximately comparable to that of **1**.[26] Our calculations have shown that **3** gives a higher barrier than **1**. *B*-allyl-1,3,2-diazaborolidine, **4**, has even a higher activation energy for the reaction with an aldehyde.

Brown and collaborators have also studied the reactivity of acyclic boronate reagents of the following structure and allylboronic acid **5**.[26]
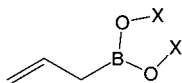
X = *n*-Pr, *i*-Pr, isopinocamphenyl, CH₂Ph

They found that among the reagents, *B*-allylbis(benzyloxy)borane and **5** are far more reactive toward benzaldehyde than the others. The present calculation suggests that **5** should be more reactive than **3** but similar in reactivity to **1** and **2**.

Electrophilicity of the Boron Atom in Allylboron Reagents. To understand the relative reactivity of allylboron reagents from a theoretical viewpoint and to develop new reagents, it will be helpful to estimate the electrophilicity of the boron center in those species. A new bond is formed between the boron atom of an allylboron molecule and the oxygen atom of the aldehyde reagent in the course of the reaction. The former serves

as an electron acceptor and the latter as an electron donor. To react with an aldehyde molecule, an allylboron molecule should provide an unoccupied orbital having a large amplitude on the boron atom. The lowest unoccupied MO is delocalized over the molecular framework, depending on the size and structure of the auxiliary. Then, to compare the reactivity of allylboron reagents of different structures, we have to take the contributions of other unoccupied MOs appropriately into account.

The bond being formed between the boron in an allylboron compound and the aldehyde oxygen is still transient at the transition state. A p-type atomic orbital (AO) of boron should play the dominant role. Now, let us produce for each allylboron molecule the orbital that has the maximum amplitude on the boron p-type AO by recombining the unoccupied MOs. For this purpose, we refer to a BH₃ molecule of a planar geometry as an ideal boron species. The boron center does not have hydrogens as the neighboring atoms in the allylborons examined in this work. The LUMO of BH₃ is a p-type orbital having a large amplitude on the boron. Another boron p-type unoccupied MO is located 0.572 au above the LUMO, and the inner and outer functions have the coefficients different in signs. The participation of this high-lying unoccupied MO in the interaction with an attacking nucleophile is weaker than that of the LUMO.[33]

Then, the unoccupied orbital of an allylboron molecule, which is closest in shape to the boron component in the LUMO of BH₃, denoted here by δ_r, is generated by projecting δ_r onto the unoccupied canonical MOs of the molecule calculated at the 6-31G** level of theory.[34,35] The resulting reactive orbital ϕ_{unoc} is given by

$$\phi_{unoc}(\delta_r) = (\sum_j^{unoc} d_{j,r}\phi_j)/(\sum_j^{unoc} d_{j,r}^2)^{1/2} \qquad (1)$$

where the denominator is the normalization factor that allows us to compare the reactivity between allylboron molecules that differ in size and structure. The coefficient $d_{j,r}$ of the canonical MO ϕ_j is determined easily by taking the inverse of the LCAO MO coefficient matrix. Here, the summation covers all the unoccupied canonical MOs. In addition to ϕ_{unoc}, the orbital δ_r has the contribution from the occupied MO space in allylboron molecules. The vacancy of the reaction site is given by $\langle\delta_r|\phi_{unoc}\rangle^2$, which is unity in the reference BH₃ molecule.

An allylboron reagent will be a strong electron acceptor when the B p-AO ($=\delta_r$) consists mainly of the unoccupied MOs and preferably of those with low orbital energies. In other words, to show a strong electrophilicity, an allylboron molecule should have the low-lying unoccupied MOs having large amplitudes on the boron center. Allylboron species examined in this study have been shown to possess practically sp² planar arrangements of bonds around the boron center in an isolated state. Then, by taking the axis of the p orbital to be equiangular from the three bonds connecting the boron atom and the adjacent atoms, the unoccupied reactive orbital has been determined for each of the allylboron reagents. The

(32) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.

(33) This has been shown by carrying out an electron configuration analysis on the system consisting of a BH₃ molecule and a H₂O molecule. It is also possible to take both of the MOs in δ_r to find the lowest value of λ_{unoc}.

(34) Fujimoto, H.; Mizutani, Y.; Iwase, K. *J. Phys. Chem.* **1986**, *90*, 2768.

(35) Fujimoto, H.; Satoh, S. *J. Phys. Chem.* **1994**, *98*, 1436.

Table 2. Electron-Accepting Level of the Projected Reactive Orbital and the Vacancy of the Reaction Site in Allylborons

compound	λ_{unoc} (au)	$\langle \delta_r | \phi_{\text{unoc}} \rangle^2$
1	0.262	0.562
2	0.268	0.559
3	0.278	0.528
4	0.288	0.505
5	0.266	0.562
6	0.240	0.567
7	0.276	0.527
8	0.235	0.556
9	0.222	0.560
10	0.242	0.565
11	0.219	0.631

vacancy of the reaction site is 0.56−0.57 in the boronates, 0.52−0.56 in the oxazaborolidines, and 0.51 in diazaborolidine, as given in Table 2. It is considerably smaller than 1. This result is natural, because the boron is in conjugation with the adjacent oxygen and nitrogen atoms in these reagents.

The electron-accepting level of the boron p-AO has been estimated then by

$$\lambda_{\text{unoc}}(\delta_r) = (\sum_{j}^{\text{unoc}} d_{j,r}^{2} \epsilon_j)/(\sum_{j}^{\text{unoc}} d_{j,r}^{2}) \qquad (2)$$

where ϵ_j signifies the orbital energy of the component MO ϕ_j.[33,34] The electrophilicity should become stronger as the λ_{unoc} value becomes smaller. It is seen that the boron atom in **1** possesses a slightly lower λ_{unoc} value than that in **2**. *B*-Allyl-1,3,2-dioxabenzoborole **6** has been shown experimentally to be much more reactive, compared to **1** and **2**.[26] Brown and collaborators suggested that the delocalization of lone pairs of electrons from the oxygen atoms onto the phenyl ring should reduce the n → p (boron) back-donation to increase the electrophilicity of the boron center. Actually, the calculated λ_{unoc} value of the boron center is lower in **6**, suggesting that **6** should be more reactive toward nucleophiles compared with **1** and **2**. It was found by Brown and collaborators that *B*-allylbis(benzyloxy)borane and **5** were far more reactive toward benzaldehyde than the others among the reagents they studied.[26] They react instantaneously with benzaldehyde at −50 °C in dichloromethane. It is not possible to ascertain from the published report how reactive **5** is, as compared with **6**. It is shown in the present analysis that **5** is similar in reactivity to **1** but less reactive than **6**.

6
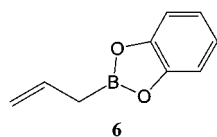
To compare the reactivity of allylborons with different types of auxiliaries, we may estimate the electrophilicity of boron toward nucleophiles by

electrophilicity of boron $\approx \langle \phi_{\text{unoc}}(\delta_r) | \delta_r \rangle^2 / \lambda_{\text{unoc}}(\delta)$ (3)

In Figure 3, one sees a nice correlation between the quantity defined by eq 3 and the calculated activation energy for the allylboron species **1**−**5** studied above, except for **11**, which will be discussed later. Boronates **1**, **2**, and **5**, which have oxygens bound to the boron
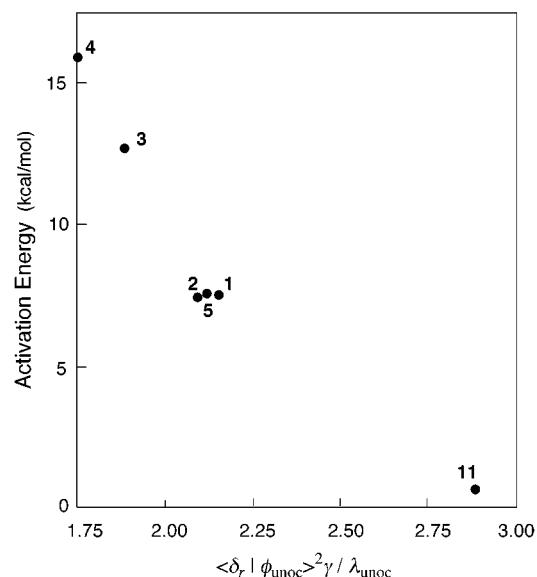

Figure 3. Relation between the calculated electrophilicity of boron in allylboron reagents and the activation energy for the reaction with formaldehyde.

center, exhibit similar reactivities to each other. *B*-allyl-1,3,2-oxazaborolidines, **3**, is seen to be less reactive than dioxaborinane or dioxaborolane, and **4**, having two nitrogens adjacent to the boron center, is even less reactive than **3** toward aldehydes.

It has been reported that the rates of reactions of the methyl- and phenyl-substituted species of oxazaborolidines **3** with benzaldehyde at 25 °C are approximately comparable to that of **1**.[26] In the present analysis, the λ_{unoc} value is considerably higher and the vacancy of the reactive orbital is smaller in **3** and its methyl-substituted species **7**, compared with **1**. It has been argued by Brown that the presence of a powerful electron-withdrawing group, such as tosyl, on the nitrogen atom may significantly enhance the electrophilicity of the reagent and greatly enhance its ability to undergo allylboration.[26] In fact, the electrophilicity has been strengthened remarkably by introducing a sulfonyl group, as in **8** and **9**. This result is in line with the experimental observation that *B*-allyl-3-(*p*-tolylsulfonyl)-1,3,2-oxazaborolidine undergoes allylboration remarkably rapidly at −78 °C.[26]

7   **8**   **9**
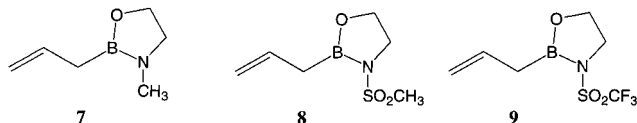
The tartrate ester (the Roush's reagent) has been shown to undergo allylboration very rapidly at −78 °C.[26] As a model, we have examined a tartaric acid **10**. It is seen that **10** should exhibit a high reactivity comparable to *B*-allyl-1,3,2-dioxabenzoborole **6** in agreement with experiments.

Roush's reagent   **10**
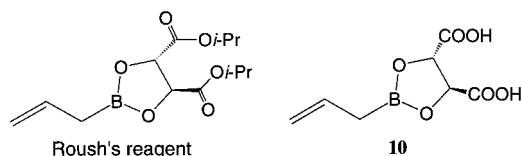
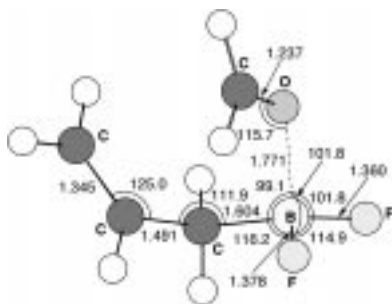Here, we may look at the species **11**, which is interesting from a theoretical viewpoint. This molecule has the

Figure 4. Structure of the complex between *B*-allyldifluoroborane and formaldehyde calculated at the MP2/6-31G** level of theory.

lowest λ_{unoc} value among the reagents studied in this work. As illustrated in Figure 3, the activation barrier evaluated from the complex does not correlate well with its reactivity predicted from the calculation of electrophilicity.
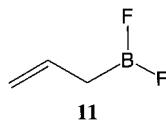

11

Figure 4 illustrates a complex formed between **11** and formaldehyde calculated at the MP2/6-31G** level of theory. It is located 10.0 kcal/mol below the initial reactants and 0.67 kcal/mol below the transition state. One sees that the B−O distance is much shorter, compared with that for the complex between **1** and formaldehyde. Naturally, the structure of the reactant is highly distorted. It is very likely that the reaction should occur without any activation energy in this case. The deviation of **11** from the linear relation between the two quantities presented in Figure 3 suggests also that the reaction should take place spontaneously. The large difference in electronegativity between boron and fluorine activates the boron in **11** by suppressing electron delocalization from the fluorine atoms to the boron atom and, therefore, by localizing the unoccupied reactive orbital effectively on the boron center. This is reasonable considering that boron fluoride BF_3 is utilized as an efficient Lewis acid in organic syntheses.

The MP2/6-31G** calculations suggest that a loose complex intervenes in the reaction of allylborons having moderately strong electrophilicity with aldehydes. In Figure 5, we show the relation between the electrophilicity scale and the energy difference between the transition state and the reactants, i.e., an allylboron molecule and a formaldehyde molecule. The energy difference was shown by taking **1** as the reference, with the transition state being 20.28 kcal/mol above the reactants at the RHF/6-31G* level and 1.73 kcal/mol above the reactants at the MP2/6-31G** level. Once again, we see a nice correlation between the two quantities for the allylborons examined above. It remains still difficult to decide whether any complex species plays an important role in determining the reactivity of allylborons. In any case, the reactivity of allylboron reagents toward aldehydes is explained in terms of the electrophilicity of the boron center estimated above.

At the transition state of allylboration, the boron center has a nonplanar arrangement of bonds, as illustrated in Figure 1. Then, to see the orbitals participating in the
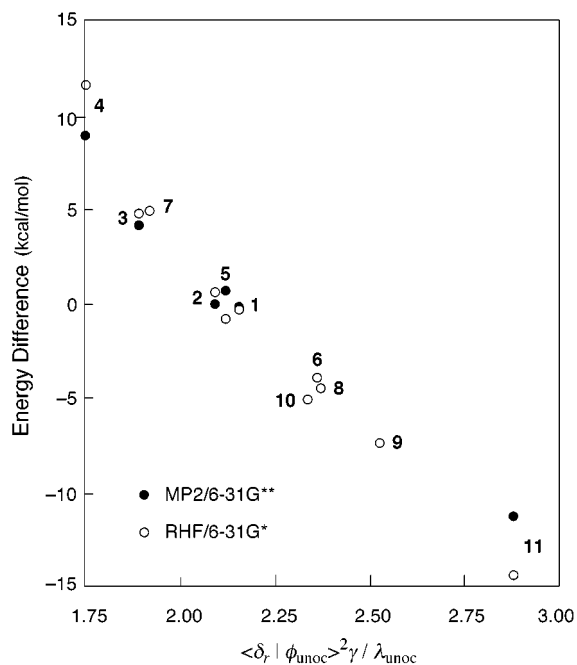

Figure 5. Relation between the calculated electrophilicity of boron in allylboron reagents and the energy difference between the transition state and the initial state in the reaction with formaldehyde. The energy difference was given by the relative value, taking the case of **1** as the standard.
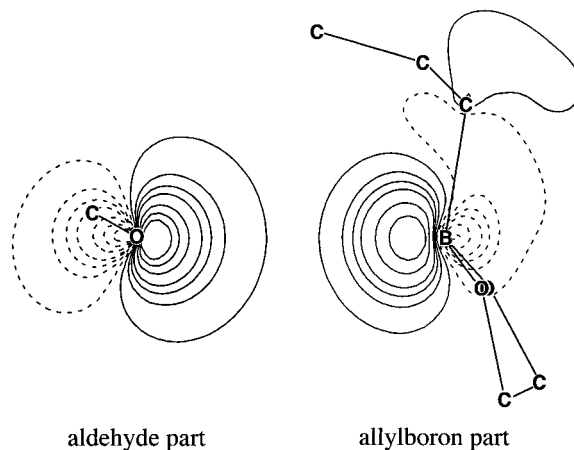

aldehyde part   allylboron part

Figure 6. Pair of interacting orbitals that plays the dominant role in electron delocalization from the aldehyde to **1**. The orbitals have been plotted in the plane defined by the boron atom and the carbon bound to the boron of **1** and the oxygen of the formaldehyde molecule. Symbols of other atoms and the bonds show their projections onto that plane.

formation of the new bond, we have carried out the transformations of MOs of the two fragment species at the transition state.[36,37] Figure 6 shows the principal pair of orbitals that represents electron delocalization from the attacking formaldehyde to **1**. The orbital of the aldehyde part is given by a combination of the occupied

(36) (a) Fujimoto, H.; Koga, N.; Fukui, K. *J. Am. Chem. Soc.* **1981**, *103*, 7452. (b) Fujimoto, H.; Koga, N.; Hataue, I. *J. Phys. Chem.* **1984**, *88*, 3539. (c) Fujimoto, H.; Yamasaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157. (d) Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578.

(37) The orbital transformations have been carried out for the occupied canonical MO space of the formaldehyde molecule and the unoccupied canonical MO space of the allylboronate molecule (see ref 36b).
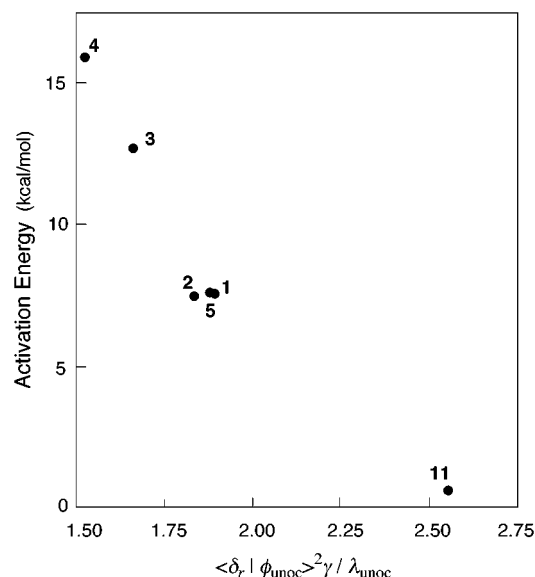
Figure 7. Relation between the reactivity scale and the activation energy for the reaction with formaldehyde. An s−p hybrid AO of boron was taken as the binding orbital.

canonical MOs of the formaldehyde molecule, being localized on the oxygen atom. The orbital of **1** is given by a combination of the unoccupied MOs, being localized well on the boron center. The s AO of the boron is seen to participate in bonding with the attacking aldehyde.

To take the contribution of the s AO into account, we have carried out an additional analysis. By taking the boron AO components of the LUMO of a BH_3 molecule having a bent structure with the H−B−H angles of 114° as the reference orbital δ_r, we have calculated the electrophilicity of boron in a similar manner. We have found again a nice correlation between the two theoretical quantities in Figure 7 for the allylboron reagents studied above. The projection of the s−p hybridized AO onto the allylboron molecules in an isolated state with a nearly planar bond arrangement around the boron center has reduced the participation of the unoccupied MOs to the hybrid AO, leading to somewhat smaller values of the electrophilicity scale compared with those presented in Figure 3. It has been shown that inclusion of the s AO elevates λ_{unoc} slightly, by ∼0.01 au, for all of the species examined here. Thus, the difference in electrophilicity between allylborons in an isolated state should be retained at the transition state to differentiate the reactivity of those reagents toward aldehydes.

Allylboronic acid **5** has been reported to be far more reactive than other allylboron reagents,[26] though the present analysis indicates that the intrinsic reactivity of boron in **5** should be comparable to that in **1**. On the other hand, the boron in the fluorinated allylboron **11** is predicted to be far more reactive toward aldehyde, compared with **1**. It is suggested, therefore, that the lone pairs of electrons have been stabilized significantly or the

conjugation between the boron and the oxygens has been weakened in the course of the reaction of **5** for some reason. For instance, the rotation of the OH groups around the B−O bonds to make the sp² lone-pair orbitals of oxygens, in place of the p-type lone-pair orbitals, conjugate with the boron p orbital leads to a marked enhancement of the electrophilicity of the boron to a magnitude comparable to that in **11**.

Conclusion

We have studied theoretically the reactivity of allylborons toward aldehydes by applying the ab initio MO method. The presence of a complex has been suggested by the calculations at the MP2/6-31G** level of theory. The interaction is very weak, however, in typical allylboron reagents, and the reactivity trend is not unchanged whether the complex is taken into account in calculating the activation energy or not. Then, we have estimated the electrophilicity of the boron atom in allylborons by projecting out the unoccupied reactive orbital having the maximum amplitude on the boron p AO. Two factors have been considered to be of importance, one being the electron accepting level of the reactive unoccupied orbital and the other being the efficiency of localization of the orbital in the unoccupied MO space. The reactivity scale taking these two factors into account has been found to be in line with the rate of allylboration observed experimentally. The theoretically estimated electrophilicity of the boron shows a nice correlation with the activation energy evaluated from the transition-state calculations. It has become clear that electron delocalization from the oxygen of an attacking aldehyde to the boron p AO governs the allylboration reaction. On the other hand, it is not clear yet if any complex species play significant roles in the reaction mechanism. We believe that the present study provides a theoretical background for the arguments developed on the basis of experiments and also will make it easier to predict the reactivity of allylboron reagents with new chiral auxiliary leading to a high diastreoselectivity.