

Mechanism of Hydroboration in Ether Solvents. A Model *ab initio* Study

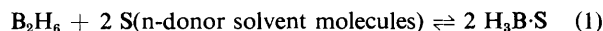
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The reaction of ethylene with an $\text{H}_3\text{B}\cdot\text{OH}_2$ complex (a model for hydroboration in ether solvents) is indicated by *ab initio* calculations to resemble an $\text{S}_{\text{N}}2$ displacement of the solvent by the olefin; the solvent plays essentially no role in the transition state, but BH_3 never becomes free during the reaction.

Olefin hydroboration in ether solvents, a rapid reaction of great synthetic utility,¹ has been well characterised kinetically.²⁻⁴ The activation energy for 2,3-dimethylbut-2-ene in tetrahydrofuran (THF) is only 9.2 kcal mol⁻¹.² In contrast, B_2H_6 reacts very slowly in the gas phase⁵ or in hydrocarbon solvents.¹ Several theoretical studies of the reaction of BH_3 with ethylene and other model olefins have been reported,⁶⁻⁹ but these bear little apparent relevance to the conditions used experimentally. Little or no activation energy is found in the gas phase for BH_3 ,⁶⁻¹⁰ but this is not the species normally present. We have now used *ab initio* molecular orbital theory†

to investigate the mechanism of the reaction of ethylene with an $\text{H}_3\text{B}\cdot\text{OH}_2$ complex. This models hydroboration in ether solvents, in which B_2H_6 is at least partially dissociated (equation 1).¹¹ The reaction product is the $\text{CH}_3\text{CH}_2\text{BH}_2\cdot\text{OH}_2$ complex (equation 2).

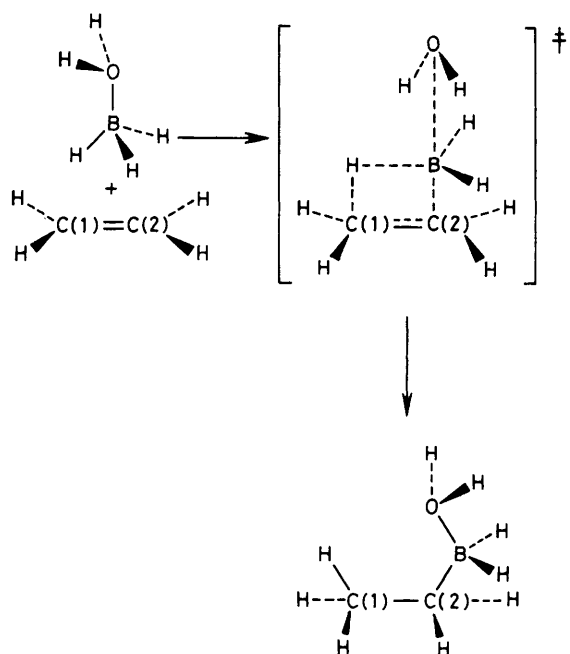


Pastor concluded that the $\text{H}_3\text{B}\cdot\text{THF}$ complex reacts directly with the olefin *via* a very early transition state in which the molecule of THF is still rather tightly co-ordinated to the boron atoms.² In contrast, Brown recently proposed dissociation of such complexes to free BH_3 prior to hydroboration.⁴ Since the complexation energy of BH_3 monomer with the solvent (equation 1) must be strong enough to overcome the dimerization energy ($2\text{BH}_3 \rightarrow \text{B}_2\text{H}_6$, -36 kcal mol⁻¹), such spontaneous dissociation is energetically implausible.

We have modelled the solution reaction for this calculation by constraining the reaction pathway to C_s symmetry and using the BC_2 distance as the reaction co-ordinate; the remain-

† All calculations used the Gaussian 76 series of programs (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, 'Quantum Chemistry Program Exchange,' Program No. 368, Indiana University, 1978). Optimizations used analytically evaluated atomic forces (H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, 1975, **63**, 3622) in a Davidon-Fletcher-Powell multiparameter search routine (W. C. Davidon, *Comput. J.*, 1968, **10**, 406; R. Fletcher and M. J. Powell, *ibid.*, 1963, **6**, 163; D. Poppinger, *Chem. Phys. Lett.*, 1975, **34**, 332).

ing geometrical parameters were optimised using the 3-21G basis set.¹²



Scheme 1

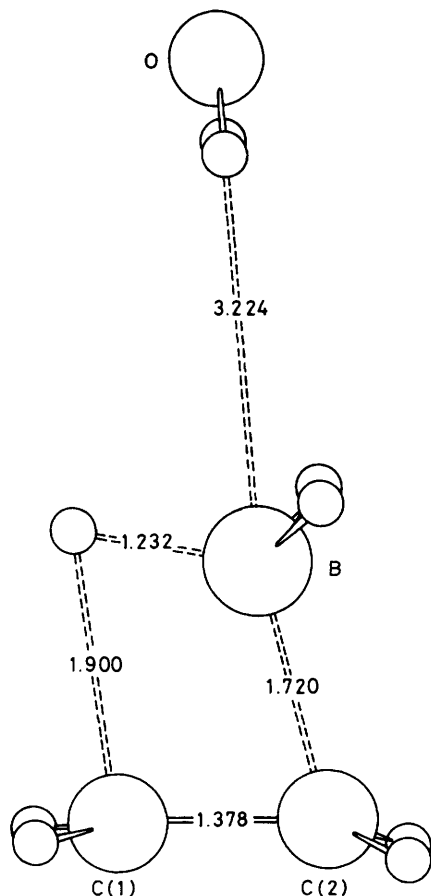


Figure 1. The 3-21G calculated maximum energy point on the reaction co-ordinate. Bond lengths are in Å.

The $\text{H}_2\text{O}\cdot\text{BH}_3$ complex approaches ethylene at a $\text{C}(1)\text{C}(2)\text{B}$ angle of *ca.* 100° initially, but this angle decreases to 80° as the displacement of the solvent proceeds (Scheme 1). The geometry of the highest energy structure located on the calculated reaction path is shown in Figure 1. The water molecule has been displaced from the borane and has turned around, *i.e.*, H_2O adopts an orientation favoured by the dipoles in the $\text{BH}_4^-\cdot\text{H}_2\text{O}$ complex. (This has the hydrogens of both molecules oriented towards each other, and an association energy of $11.8 \text{ kcal mol}^{-1}$ at 3-21G or 3-21+G.) In the real reaction with ethers, the solvation of the transition state should be minimal. Moreover, the $\text{BH}_3\cdot\text{C}_2\text{H}_4$ unit in Figure 1 resembles the 4-31G transition state for the 'gas phase' $\text{BH}_3 + \text{ethylene}$ reaction found by Morokuma *et al.*;⁸ the H_2O contribution is not significant. The molecular orbital changes during the reaction are analogous to those outlined earlier for the gas phase reaction⁶ except that the initial donor-acceptor interaction between olefin HOMO and BH_3 LUMO has been replaced by less favourable nucleophilic interaction with the $\sigma_{\text{B}^*}^*$ orbital of the $\text{BH}_3\cdot\text{H}_2\text{O}$ complex. The displacement of the water is essentially complete before the second stage of the reaction, the donation from the BH_3 HOMO to the ethylene LUMO,⁸ becomes important. Despite an extensive search, we were unable to find a transition state in which the solvent molecule is still associated appreciably with the borane, as suggested by

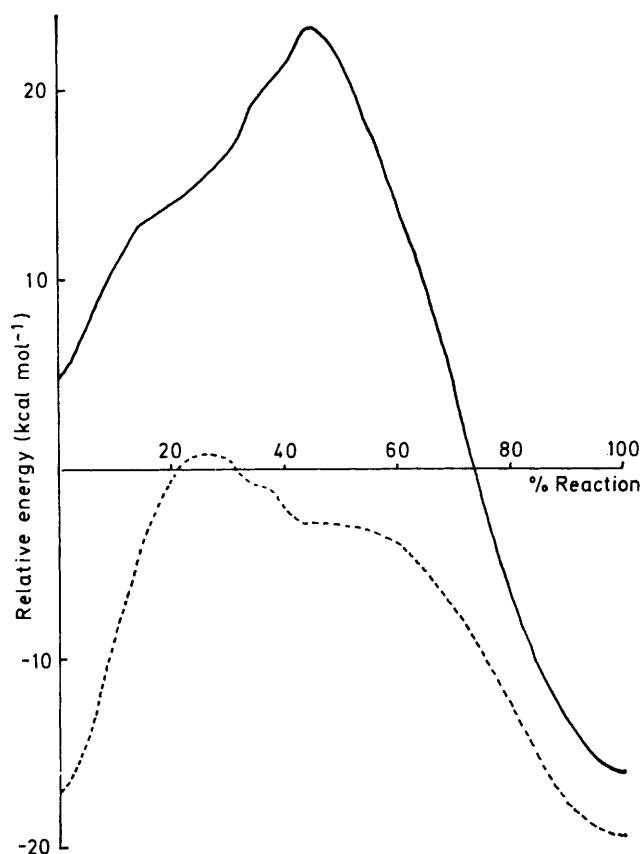


Figure 2. Energy profiles for the reaction of $\text{H}_3\text{B}\cdot\text{H}_2\text{O}$ with ethylene. The '% Reaction' co-ordinate is the arithmetic mean of the % reaction parameters for the CC , $\text{C}(2)\text{B}$, BH , and $\text{C}(1)\text{H}$ bond lengths; H is the unique hydrogen and 0% reaction is defined for a $\text{C}(2)\text{B}$ distance of 2.8 \AA . This reaction co-ordinate gives smoother curves than those involving individual variables. The solid line shows the reaction profile (relative to $\text{H}_3\text{B}\cdot\text{H}_2\text{O} + \text{C}_2\text{H}_4$) and the dashed line the solvation energy during the reaction. Note that H_2O is only weakly bound during most of the reaction and at the transition state. H_2O is strongly bound to BH_3 and to the product $\text{C}_2\text{H}_5\text{BH}_3$.

Pasto *et al.*² However, Pasto's description is largely confirmed by our calculations; the olefin displaces the solvent from its association complex with BH_3 . The main contributor to the activation barrier is the energy required to overcome the association energy of the solvent with BH_3 in the solvent-borane complex. The transition state involves a four centre-four electron C-C-B-H interaction, as in the gas phase.

The 3-21G calculated activation energy for the reaction of $\text{BH}_3 \cdot \text{H}_2\text{O}$ with ethylene, $30.2 \text{ kcal mol}^{-1}$, is probably too high for several reasons. The C_s symmetry constraint employed may have led to a higher activation energy than that for full optimisation. The size of the system precludes a more thorough search for the transition structure. In any event, the difference between our model reaction and experiment is large. The greatest source of error is, however, the overestimation of the $\text{BH}_3 \cdot \text{H}_2\text{O}$ complexation energy at 3-21G. Hence, we performed single point calculations on the 3-21G optimised geometries using the diffuse function-augmented 3-21+G basis set,¹³ which provides an improved description of the oxygen lone pairs.¹⁴ The resulting energy profile is shown in Figure 2, and gives a more reasonable activation energy ($23.3 \text{ kcal mol}^{-1}$).

Figure 2 also shows the calculated solvation energy of the points on the reaction path, and confirms the nearly complete dissociation of the solvent during the reaction. The small (*ca.* 3 kcal mol^{-1}) solvation energy at the transition state is due to the $\text{BH}_4^- \cdot \text{H}_2\text{O}$ type interaction. The solvation energy increases after the transition state as the reaction proceeds towards the $\text{C}_2\text{H}_5\text{BH}_2 \cdot \text{OH}_2$ product.

Our calculations support Brown's contention⁴ that the solvent plays no role in the transition state, but disagree with his reasoning. The dissociation of the BH_3 -solvent complex does not occur spontaneously, but requires the participation of the olefin. The vacant p-orbital of BH_3 must always be engaged; in B_2H_6 , in the BH_3 -solvent complex, and in the hydroboration transition state.

Brown's model is S_N1 -like. Instead, we agree with Pasto that the process is an S_N2 -like nucleophilic displacement on boron, but with a late rather than an early transition state. We agree with Brown that the solvent in BH_3 -solvent complexes provides a better leaving group than the second BH_3 in B_2H_6 . The 'enormous catalytic effect of THF on the rate of hydroboration of alkenes with diborane'⁴ is easily explained. If no association complex is formed (as in hydrocarbon solvents) or the equilibrium in equation 1 lies too far to the left, the reaction will be very slow. If, however, the $\text{H}_3\text{B} \cdot \text{S}$ complex is too tightly bound, the rate of reaction 2 will be too low as a consequence. Many examples are known.⁴ The best accelerating solvents are those which form complexes with BH_3 of intermediate energy (the equilibrium of equation 1 is neither very far to the left nor to the right), but are displaced easily by olefins.

A further consequence of these conclusions is that calculations on 'gas phase' reactions of BH_3 with olefins should be reasonable models for hydroboration in solution, *e.g.*, as far as the stereoselectivity is concerned.^{9,15} We note that the complexes of more hindered boranes, such as 9-borabicyclo[3.3.1]nonane,⁴ may be expected *not* to undergo S_N2 -like displacements by olefins, and may well react by a different mechanism.

This work was supported by the Fonds der Chemischen Industrie. We thank the staff of the Regionales Rechenzentrum Erlangen for their co-operation.

Received, 28th February 1983; Com. 272

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