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HYDROBORATION; AN AB INITIO STUDY OF THE REACTION OF BH_3 WITH ETHYLENE *

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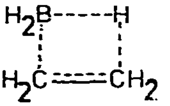
Summary

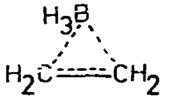
Ab initio molecular orbital calculations indicate the reaction of BH_3 with ethylene to proceed exothermically via an intermediate π-complex, but without an overall activation barrier. The mechanism of the reaction in the gas phase is indicated to proceed in two facile stages: the formation of the π-complex and its rearrangement to ethyl borane product. The progress of the reaction is shown pictorially by drawings of the interacting orbitals at various stages.

Introduction

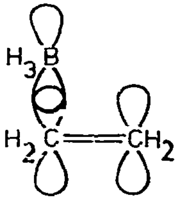
Brown and Subba Rao's discovery of hydroboration [1] led to intense activity in developing synthetic applications of this reaction [2,3]. However, the detailed mechanism of hydroboration is still not well defined, although there has been much qualitative discussion. Brown and Zweifel's proposal of a four-center transition state (I) [4] was a logical consequence of the observation that hydroboration is a *cis* 1,2 addition. Seyferth [5] and Streitwieser [6] have suggested that a π-complex (II) may intervene as an intermediate in this process. Jones [7] considered the concerted 1,2 addition of a BH bond to a CC multiple bond (I) to be



(I)



(II)



(III)

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[*] Dedicated to Professor H.C. Brown in recognition of his contributions to chemistry.

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a forbidden process, but rearrangement of II to product IV to be symmetry allowed. However, the involvement of the vacant orbital on boron (III) would make the concerted four-center process allowed [8,9], and Brown's original suggestion (I) cannot be excluded on an orbital symmetry basis.

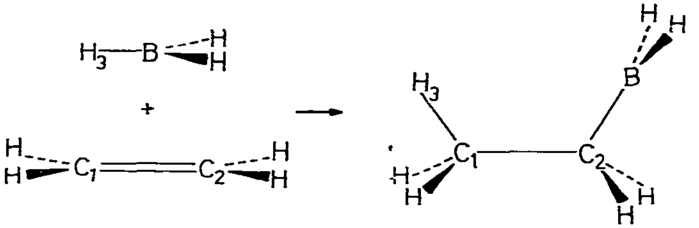
The hydroboration reaction is complicated by a strong tendency of the borane to dimerize or to form a complex with the solvent. For instance, the reaction of $BH_3 \cdot THF$ with 2,3-dimethylbut-2-ene is first order in both the borane complex and the olefin [8], whereas the reaction of disiamylborane dimer with olefins is first order in the borane dimer [10]. In the former case the reaction occurs via a solvated borane monomer, but this can be ruled out for the second reaction. The kinetics of the gas phase reaction of diborane with ethylene were originally interpreted in terms of a mechanism involving prior dissociation of the diborane [11], but Pasto [8] has pointed out that the proposed mechanism is inconsistent with the observed very rapid rate of reaction of BH_3 monomer with ethylene [12]. Thus, there are really three mechanisms to be considered involving multiple bond additions of (1) borane monomers, (2) borane dimers, and (3) solvated or complexed boranes.

We have now used ab initio molecular orbital theory to investigate the mechanism of the simplest of these processes, the gas phase reaction of BH_3 with ethylene. During the course of our work, Dewar and McKee's similar study of this reaction using the MNDO semi-empirical method came to our attention [13].

Method

Single determinant SCF molecular orbital theory in its spin-restricted form (RHF) was used throughout [14], employing the STO-3G [15] minimal and 4-31G [16] split-valence basis sets. The reaction pathway considered was confined to C_s symmetry (Scheme 1) in order to simplify the computational task.

SCHEME 1



(1)

Geometry optimization employed the Davidon—Fletcher—Powell multiparameter gradient optimization method [17]. The intermediate π-complexes (IIa and IIb) were completely optimized within the constraints of C_s symmetry at both RHF/STO-3G and RHF/4-31G levels.

The choice of the reaction coordinate (i.e. the parameter to be fixed during optimization of a non-equilibrium geometry) is critical for this reaction. The C^2—B distance or the C=C bond-center to B distance are both relatively insensitive to a circling motion of the boron around C^2. We have therefore used the C^2C^1B angle, θ, as the reaction coordinate (see Scheme 1). (The points at greater BH_3 to C=C distances than that in the π-complex actually were obtained by fixing the perpendicular C=C to B distance, which is almost equivalent to fixing θ at these intermolecular separations, but which leads to faster optimization.) The ethyl borane isomers (IVa—IVd) were completely optimized, each within the constraints of C_s symmetry.

Results and discussion

The RHF/STO-3G geometries and total energies of the calculated hydroboration path are shown in Tables 1, 2 and 3 and in Fig. 1.

In proceeding from the separated reactants, two minima are found on the C_s energy surface: the π-complex II and the product, ethyl borane IVa. In contrast to the MNDO study of Dewar and McKee [13], no barrier to the formation of the π-complex II was found. The three alternative conformations of ethyl borane (IVb—IVd) have been investigated and, contrary to conclusions derived from earlier standard geometry calculations [18], IVd is found to be the most stable isomer, rather than IVb. The enthalpy of hydroboration of ethylene by BH_3 monomer to yield VId is found to be —63.1 kcal mol^{-1} at RHF/STO-3G and —32.5 kcal mol^{-1} at RHF/4-31G (with the STO-3G optimized geometries). This latter value is in good agreement with an average experimental gas phase

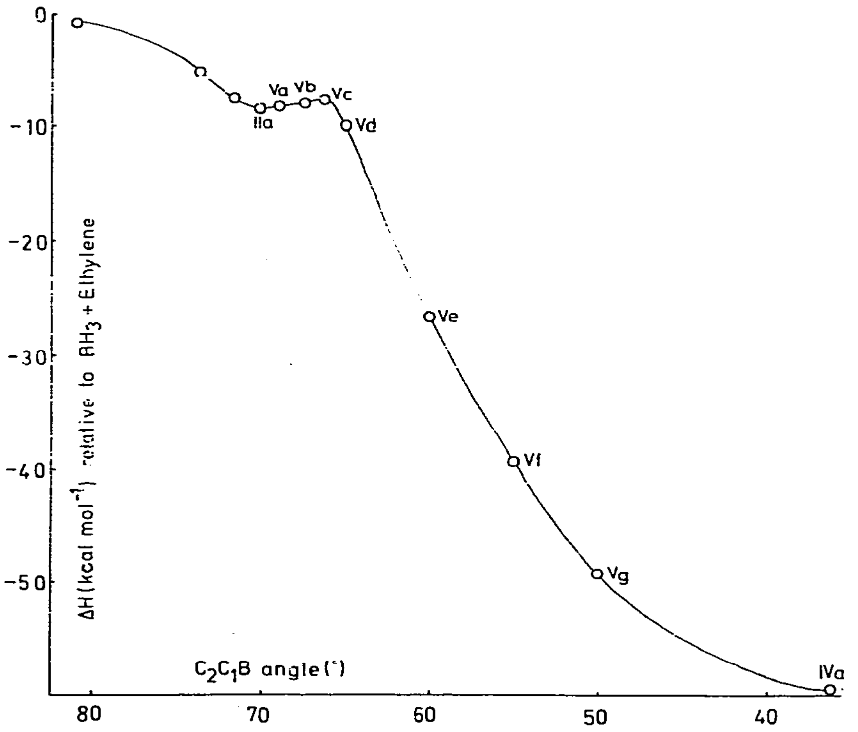


Fig. 1. The RHF/STO-3G energy profile for the reaction of monomeric borane (3) with ethylene within the constraints of C_S symmetry (Scheme 1).

value derived from Scheme 2:

SCHEME 2

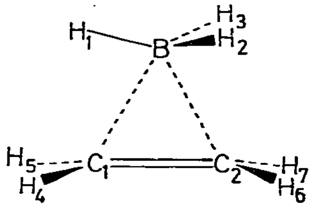
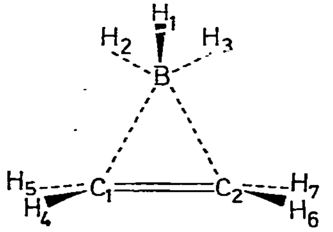
$$\begin{array}{lllll} & BH_3 & + \; 3\,C_2H_4 & = \; (C_2H_5)_3B & \\ \Delta H_f^0 = & +23\ [19] & +12.5\ [20] & -36.5\ [20] & \text{kcal mol}^{-1} \end{array}$$

$H^0_{\text{react}} = -97$ kcal mol^{-1} (average for each step = -32.3 kcal mol^{-1})

The reaction profile (Fig. 1) shows that the hydroboration reaction proceeds without overall activation energy, and that the rearrangement of the intermediate π-complex to ethyl borane has an activation barrier of only 0.32 kcal mol^{-1} (RHF/STO-3G). The transition state for this step involves only a weak three-center two electron bond rather than four-center bonding, and resembles II rather than I or III. We emphasize that ab initio calculations at the levels em-

TABLE 1

π-COMPLEX OPTIMIZED GEOMETRIES [a]

Species	Basis set	C^1B	C^2B	C^1C^2	BH^1	BH^2
BH_3, D_{3h} [25]	STO-3G 4-31G				1.160 1.183	1.160 1.183
C_2H_4, D_{2h} [26]	STO-3G 4-31G			1.306 1.316		
 IIa, Cs	STO-3G 4-31G	2.067 2.844	2.046 2.844	1.335 1.322	1.160 1.184	1.156 1.185
 IIb, Cs	STO-3G 4-31G	2.087 2.844	2.087 2.844	1.342 1.324	1.155 1.182	1.158 1.187

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[a] Bond lengths in Å, angles in degrees. XH_2 group geometries are indicated by the YXH_{nm} angle, which is the angle between the XY bond and the H_nXH_n plane, and by the H_nXH_n angle. [b] For IIa ϕ is the C^1BH^1 angle, for IIb the H^1BC^2 angle.

ployed here are not to be considered quantitatively definitive since the possible effects of polarization functions and of electron correlation are not included. However, the trends found should be accurate.

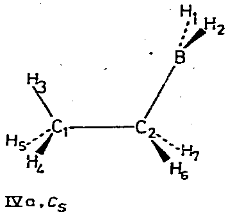
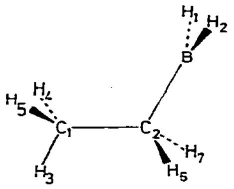
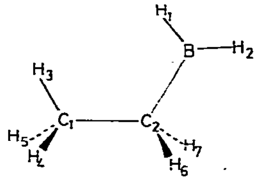
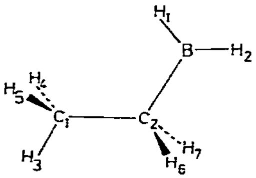
At RHF/STO-3G the binding energy of the π-complex IIa is -8.0 kcal mol^{-1} and that of its rotamer IIb is -7.8 kcal mol^{-1}. As the geometries and energies of such complexes are known to be extremely basis set dependent [24], IIa and IIb were optimized at the RHF/4-31G level. The results, shown in Table 1 indicate looser π-complexes with binding energies of -3.0 kcal mol^{-1} for both IIa and IIb. The geometries of the BH_3 and C_2H_4 moieties in their complex show smaller deviations from the structures of the isolated reactants than at the minimal basis set level. Nevertheless the π-complexes are still found to be local minima at the RHF/4-31G level; i.e. there is a barrier to rearrangement of II to ethyl borane at both minimal and split-valence basis set levels.

The reaction profile shown in Fig. 1 is consistent with the kinetic data of Fehlner [12], who found the activation energy for the gas phase reaction of

C^1H^4	C^2H^6	$C^2C^1H^{4,5}$	$C^1C^2H^{6,7}$	ϕ^b	$H^1BH^{2,3}$	H^2BH^3	$H^4C^1H^5$	$H^6C^2H^7$
					180.0	120.0		
					180.0	120.0		
1.084	1.084	180.0	180.0				115.6	115.6
1.073	1.073	180.0	180.0				116.0	116.0
1.084	1.083	173.3	171.8	20.9	143.8	118.4	116.5	116.3
1.072	1.072	179.2	179.1	15.8	172.2	120.3	116.2	116.0
1.083	1.083	173.1	173.1	101.7	146.9	114.0	116.4	116.4
1.072	1.072	179.1	179.1	92.4	171.8	119.5	116.2	116.2

TABLE 2

ETHYL BORANE STO-3G OPTIMIZED GEOMETRIES [a]

Conformation	C^1C^2	C^2B	BH^1	BH^2	C^1H^3	C^1H^4	C^2H^6
 IVa, C_s	1.564	1.574	1.162	1.162	1.088	1.085	1.085
 IVb, C_s	1.552	1.576	1.162	1.162	1.087	1.086	1.086
 IVc, C_s	1.552	1.574	1.162	1.163	1.085	1.086	1.089
 IVc, C_s	1.543	1.575	1.162	1.163	1.086	1.087	1.090

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[a] Geometries defined as in Table 1. [b] For IVa and IVb ϕ is the C^2BH^{12} angle (bent towards C^1); for IVc and the C^2BH^1 angle.

monomeric BH_3 with ethylene to be 2 ± 3 kcal mol^{-1}. Fehlner also suggested that the reaction proceeds via a loose π-complex, as indicated by our results.

A correlation diagram for the reaction is shown in Scheme 3. The changes in the molecular orbitals formed from the frontier orbitals of the reactants during

C^1C^2B	H^1BH^2	ϕ [b]	$C^2C^1H^3$	$C^2C^1H^{4,5}$	$C^1C^2H^{6,7}$	$H^4C^1H^5$	$H^6C^2H^7$
108.1	119.6	177.1	112.6	127.1	123.3	107.3	108.0
109.2	118.6	177.8	110.3	127.9	121.9	108.1	107.7
117.2	118.7	122.2	111.7	123.6	123.6	107.7	104.6
116.1	118.6	122.0	111.0	127.3	123.3	107.9	105.1

hydroboration can be followed [21] by means of the three dimensional MO plots shown in Fig. 2 [22]. The dominant interaction in the early stages of the reaction, between the ethylene π-HOMO and the vacant boron *p*-orbital LUMO (Fig. 2a), leads to the formation of the π-complex IIa, in which the three-center

(continued on p. 201)

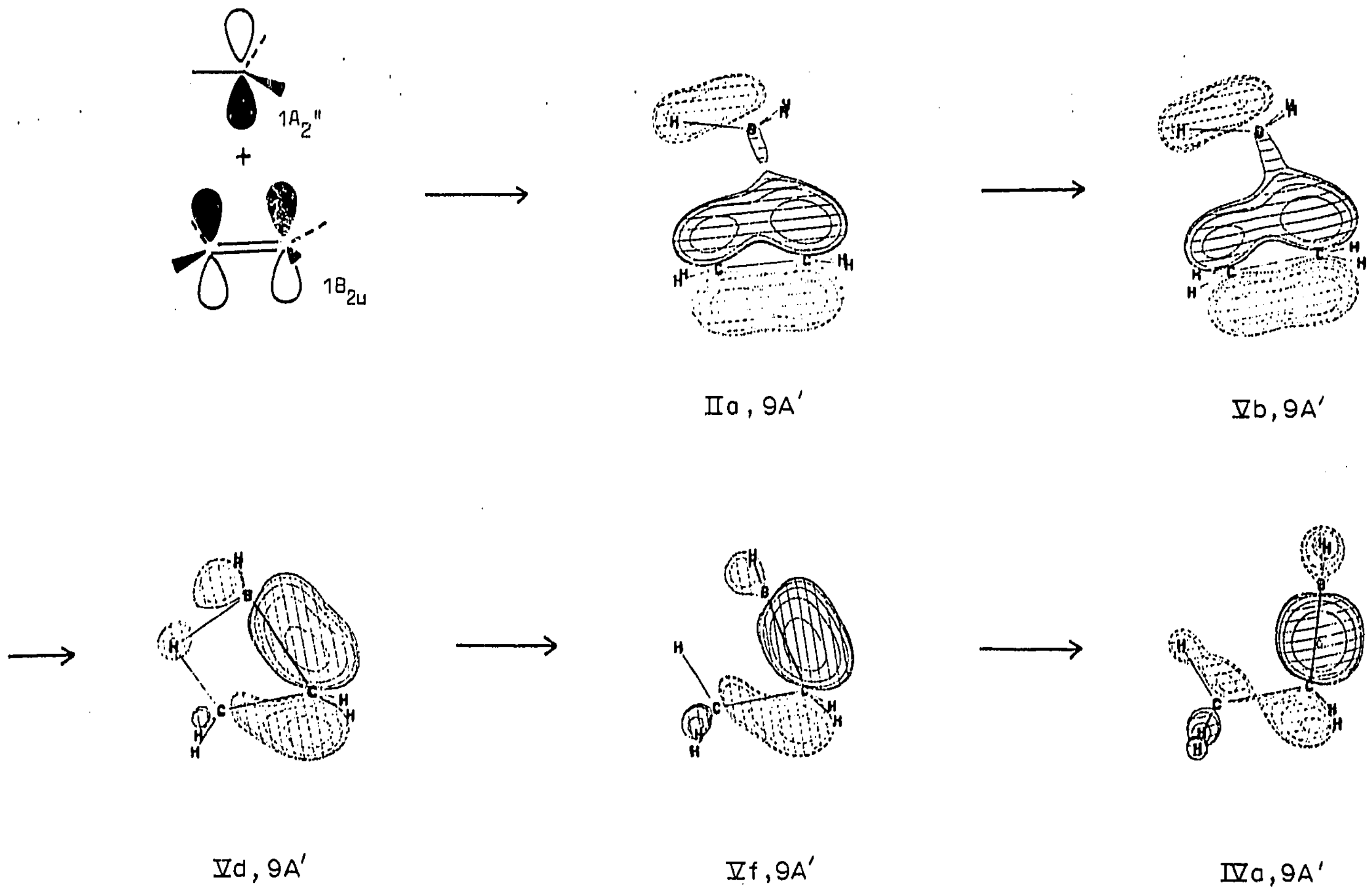


Fig. 2A.

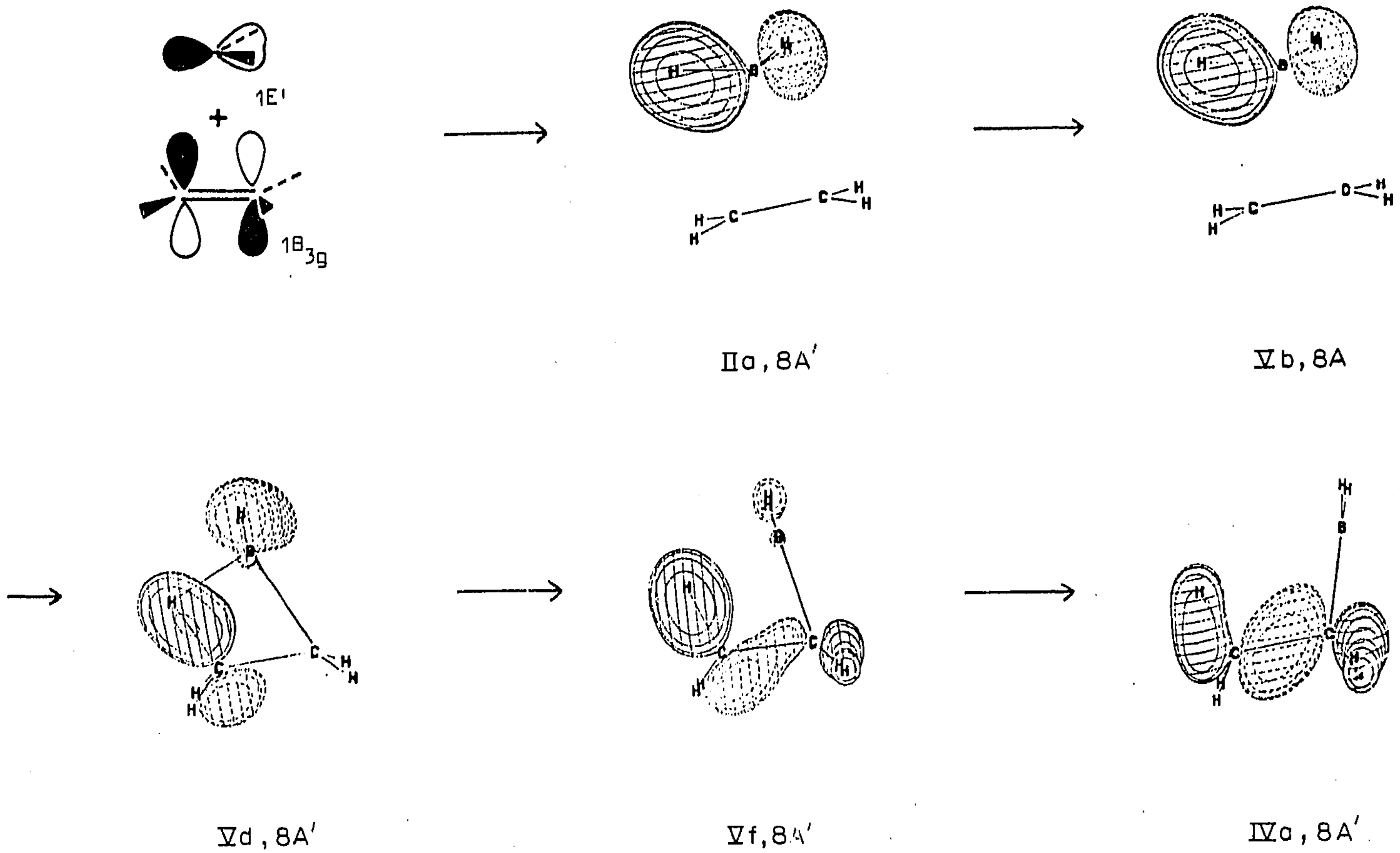


Fig. 2. Three dimensional molecular orbital plots of the orbitals formed by the interaction of the frontier orbitals of BH_3 and ethylene throughout the reaction. The numbering of the species Vb—Vf is shown in Fig. 1.

TABLE 3

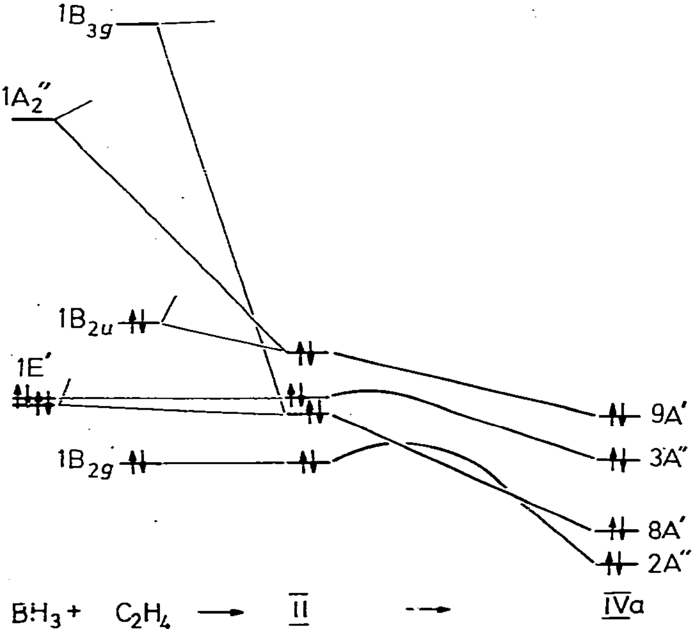
RHF/STO-3G AND RHF/4-31G TOTAL ENERGIES

Species	Total energy (atomic units [a])		
	STO-3G opt. geometry		4-31G opt. geometry
	STO-3G	4-31G	
BH_3 [25]	−26.07070	−26.34845	−26.34927
C_2H_4 [26]	−77.07396	−77.92188	−77.92216
Va	−103.14575		
Vb	−103.15279		
Vc	−103.15636		
IIa	−103.157[illegible]		−104.27619
IIb	−103.15712		−104.27618
VIa	−103.15729		
VIb	−103.15698		
VIc	−103.15878		
VId	−103.16321		
VIe	−103.18679		
VIf	−103.20724		
VIg	−103.22291		
IVa	−103.23970	−104.31648	
IVb	−103.24417	−104.32058	
IVc	−103.24071	−104.31823	
IVd	−103.24517	−104.32218	

[a] 1 au = 627.49 kcal mol^{-1}.

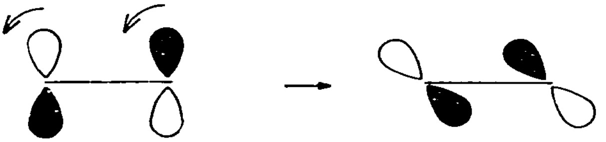
SCHEME 3

Correlation diagram for the reaction of monomeric borane (3) with ethylene. The energy (vertical) scale is arbitrary. The 8A′ and 9A′ orbitals are shown in Fig. 2. The 2A″ and 3A″ orbitals are π-CH_2 and π-BH_2 orbitals, which are not directly involved in the reaction.



bonding and rehybridization at boron is easily seen. In IIa, the interaction of the ethylene π^*-LUMO with one of the degenerate BH_3 HOMO's (Fig. 2b) is scarcely discernible. This interaction is, however, strong enough to favor the π-complex IIa over its rotamer IIb [9]. The donor—acceptor HOMO of the π-complex (IIa, Fig. 2a) is then smoothly converted (via Vb—Vf) to a C—B bonding orbital (IVa). At C^2 (for numbering see Scheme 1), the contribution of the p_z orbital changes very little. At C^1, the overall effect amounts to a rotation of the original p_z orbital resulting in a change in phase in IVa, allowing C^1—H^3 bonding. The interaction of one of the BH_3 HOMO's with the ethylene LUMO (Fig. 2b) becomes progressively more important as the reaction proceeds, as it eventually leads to C^1—H^3 bonding. This amounts to a tipping of the π^* ethylene orbital (shown in Scheme 4) during reaction. As the vacant boron p-orbital in BH_3 is occupied in both diborane [22] and in $BH_3 \cdot$ solvent complexes [23,24], the mechanisms of the reaction of borane dimers and of solvated boranes with carbon multiple bonds must be somewhat different from those for the simpler case considered here. In view of our results for the $BH_3 + C_2H_4$ reaction, it appears that the activation barrier in solution [8] must, in part, be due to the partial displacement of solvent from its borane complex, an endothermic process. The binding energy of water to BH_3 at the RHF/4-31G level is —11.0 kcal mol^{-1} [24], compared with —3.0 kcal mol^{-1} for the BH_3 + ethylene complex at the same level (Table 3).

SCHEME 4



Our results do not pertain directly to the selectivity of hydroboration, but it is unlikely that a reaction with no overall activation energy could be selective. Dewar [13] has suggested that gas phase hydroboration with BH_3 monomer should display no selectivity, and that the observed selectivity of the reaction in solution is a consequence of the solvent coordination introducing an activation barrier. Although we have not yet studied substituted ethylenes, our results for the parent reaction support this view.

Acknowledgements

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Note added in proof. A recently published CNDO/2 study of the reaction of ethylene with borane concludes that a "3-center transition state" (cf. II) is preferred to one involving four centers (cf. I) [27]. It is not clear to us how the geometries of these "complexes" were "fully optimized". We found no static point, neither a local minimum nor a saddle point, corresponding to I on the reaction energy surface. Our transition state (Vc) resembles π complex IIa closely in structure and in energy.