electrons from the Rh d_{z^2} orbital through the strong bonding interaction between CO_2 $\pi_{\|}^*$ and Rh d_{z^2} orbitals, leading to significant stabilization of the Rh d_{z^2} orbital. On the other hand, the NH_3 ligand has a lone pair and is a typical Lewis base, which destabilizes the doubly occupied d_{z^2} orbital with a four-electron destabilizing interaction between these two orbitals. $RhCl(AsH_3)_4(CO_2)$ can be viewed as a charge-transfer complex between carbon dioxide and $RhCl(AsH_3)_4$, because of a significant charge transfer from Rh to carbon dioxide. Such a significant charge-transfer interaction accumulates electrons on the terminal oxygen atoms. Simultaneously, this interaction raises the energy level of π and $n\pi$ orbitals of carbon dioxide and increases the oxygen p_π contribution to the HOMO originating mainly from the Rh d_{z^2} orbital. Consequently, the electrophilic attack to the oxygen atom of CO_2 is much enhanced in $RhCl(AsH_3)_4(CO_2)$. On the other hand, little charge transfer occurs in $(NH_3)(CO_2)$, where the complexed carbon dioxide is much less reactive with an electrophile than the carbon dioxide of $RhCl(AsH_3)_4(CO_2)$.

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Electron Correlation Effects on the Ground-State Structure and Stability of Triborane(9)

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Coupled-cluster and many-body perturbation (MBPT) theories are applied to a study of the ground-state structure and thermodynamic stability of triborane(9). Electron correlation effects are shown to have a dramatic influence on the predicted equilibrium structure of B_3H_9, shortening the nominally nonbonded B···B distances by 0.15 Å relative to the minimum-energy self-consistent-field structure. Reaction energies for $B_2H_6 + BH_3 \rightarrow B_3H_9$ are also sensitive to correlation effects, which stabilize the product by approximately 20 kcal/mol. For a [4s3p1d]/[3s1p] Gaussian basis set, the MBPT(4) electronic reaction energy is −7.9 kcal/mol. Introduction of thermal and entropic effects, however, favors the reactants. At room temperature, the Gibbs free energy change for the reaction is predicted to be +4.6 kcal/mol, suggesting that B_3H_9 does not serve to trap BH_3 during the pyrolysis of diborane.

Introduction

Although triborane(9) (see Figure 1) has not been characterized experimentally, its formation and subsequent destruction are believed to play an important role in the pyrolysis of diborane (B_2H_6). The mechanism for this important sequence of reactions, which served as the original synthetic route to the higher boranes,[1] has not been unambiguously determined. It is widely believed, however, that the process is initiated by the three elementary reactions[2]

$$B_2H_6 \rightleftharpoons 2BH_3 \tag{1}$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \tag{2}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{3}$$

with either step 2 or 3 rate-limiting. The ephemeral existence of a triboron hydride has been supported by mass spectroscopy,[3] but no thermochemical or kinetic information pertaining to reactions 2 and 3 exists. Consequently, ab initio calculations appear to provide the most suitable means for studying this important process. Here too, however, the boranes present a problem. The quasi degeneracy of the boron 2s and 2p atomic orbitals leads to a number of configurations that make important contributions to the exact molecular wave function. Hence, the simple molecular orbital description is not suitable for *quantitative* theoretical studies of this class of compounds. Recent advances in quantum-chemical theory and computational speed have made the calculation of highly correlated molecular wave functions routinely possible for small to moderately sized systems. In the past few years, we have carried out large-scale calculations on a number of electron-deficient molecules, including BH_3 and B_2H_6,[4] B_2H_4,[5] and BeB_2H_8.[6] Currently, our efforts are directed toward application of these techniques to the diborane pyrolysis mechanism. In this paper, we report results of recent calculations on the ground-state structure and energy of triborane(9), a molecule that has proven to be unusually sensitive to electron correlation effects.

Calculations

Calculations reported here were carried out with the ACES program system, developed by Bartlett and collaborators.[7] Two basis sets have been used in this study: the fully polarized [3s2p1d]/[2s1p] and [4s3p1d]/[3s1p] sets used by Redmon, Purvis, and Bartlett[8] [hereafter termed (321/21) and (431/31)]. In addition, some calculations were performed with a basis derived from (321/21) by deleting the hydrogen polarization functions [(321/2)]. Unconstrained geometry optimizations of B_3H_9 (as well as B_2H_6 and BH_3) were performed with both basis sets at two levels of theory: the self-consistent-field (SCF) approximation and many-body perturbation theory,[9] carried out to second order [MBPT(2)]. At (321/21)-MBPT(2) equilibrium geometries, energy differences were calculated at a variety of highly correlated levels: MBPT through full

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[⊥] Auburn University.

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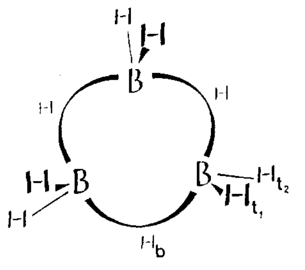

Figure 1. The triborane(9) molecule. The symmetrically equivalent H_b and H_{t2} atoms lie below the plane formed by the boron atoms, while the H_{t1} atoms are above.

Table I. Optimized Geometrical Parameters for Borane(3), Diborane(6), and Triborane(9) at both SCF and MBPT(2) Levels[a] (Distances in Angstroms; Angles in Degrees)

	SCF		MBPT(2)	
	(321/2)	(321/21)	(321/2)	(321/21)
		BH_3		
r(B–H)	1.195	1.194	1.200	1.196
		B_2H_6[b]		
r(B–B)	1.795	1.794	1.776	1.780
r(B–H_t)	1.190	1.189	1.195	1.192
r(B–H_b)	1.331	1.330	1.329	1.323
∠(H_t–B–H_t)	122.5	122.4	122.9	122.9
		B_3H_9[c,d]		
r(B–B)	2.184	2.168	2.010	2.018
r(B–H_{t1})	1.184	1.183	1.189	1.185
r(B–H_{t2})	1.195	1.194	1.206	1.202
r(B–H_b)	1.307	1.306	1.309	1.302
Δ(H_{t1})	1.140	1.136	1.131	1.125
Δ(H_{t2})	0.878	0.880	0.878	0.889
Δ(H_b)	0.356	0.365	0.467	0.457

[a] Basis sets are described in the text. [b] t and b refer to terminal and bridge hydrogen atoms, respectively. [c] Atomic designation is consistent with Figure 1. [d] Δ is the distance between the atom and the plane defined by the boron atoms.

fourth order, including effects of triply excited Slater determinants, and two levels of the coupled-cluster (CC) approximation,[10] CCSD[11] and CCSD+T(CCSD).[12] These methods treat the effects of singly and doubly excited determinants to infinite order in perturbation theory. The latter of the two also approximates the contribution of triple excitations to the correlation energy. Recent comparisons with full configuration interaction calculations, which provide exact solutions to the Schrodinger equation specified by the Born–Oppenheimer Hamiltonian within the space spanned by the basis set, suggest that CCSD+T(CCSD) correlation energies are within a few percent of the exact values for molecules near their equilibrium geometries.[12-14] A principal advantage of CC schemes is that contributions from all excitation levels enter the CC wave function, unlike truncated configuration interaction methods. This property is due to the exponential nature of the CC wave operator and is discussed in great detail elsewhere.[10] Both MBPT and CC methods satisfy the linked-cluster theorem,[15] ensuring that resulting energies are "size-extensive"—that is, they scale linearly with the size of the system. Consequently, these methods are particularly suitable for studies of chemical reactions.

Due to the large number of basis functions in the B_3H_9 calculations [90 with the (321/21) basis, 111 with (431/31)], selected molecular orbitals were not included in the highly correlated calculations presented in the following section. The three K-shell MOs which roughly correspond to the boron 1s atomic orbitals were omitted from calculations in which both basis sets were used, while three virtual functions with orbital eigenvalues greater than 18 au were dropped when the (431/31) basis was used.

Table II. Theoretical Values of ΔE_e for the Borane(3) Addition Reactions $2BH_3 \rightarrow B_2H_6$ (I) and $BH_3 + B_2H_6 \rightarrow B_3H_9$ (II) Calculated at Various Correlated Levels with the (321/21) and (431/31) Basis Sets[a] (kcal/mol)

	I		II	
	(321/21)	(431/31)	(321/21)	(431/31)
SCF	-21.2	-21.2	11.5	13.9
MBPT(2)	-40.9	-41.2	-11.1	-9.0
MBPT(2)[a]	-40.8	*b*	-9.2	*b*
MBPT(3)	-39.2	-39.2	-8.7	-6.6
D-MBPT(4)	-38.4	-38.6	-8.1	-6.1
SD-MBPT(4)	-38.8	-39.1	-8.6	-6.6
SDQ-MBPT(4)	-37.9	-38.2	-7.4	-5.4
MBPT(4)	-39.6	-40.2	-9.7	-7.9
CCSD	-37.3	*c*	-6.8	*c*
CCSD+T(CCSD)	-39.3	*c*	-9.3	*c*

[a] Boron K-shell molecular orbitals and corresponding virtual functions were omitted from the correlated calculations. [b] Calculated at optimized (321/21) SCF geometries. [c] Calculation not performed.

Results

Optimized internal coordinates for BH_3 (D_{3h} symmetry), B_2H_6 (D_{2h}), and B_3H_9 (C_{3v}) are listed in Table I. In agreement with studies using other basis sets,[16] introduction of electron correlation at the MBPT(2) level has only a modest effect on the structures of BH_3 and B_2H_6. Inspection of the internal coordinates for B_3H_9, however, reveals a significant shortening of the nominally nonbonded $B\cdots B$ distances. With the fully polarized (321/21) basis set, the MBPT(2) distance of 2.018 Å is 0.150 Å shorter with the corresponding SCF value, and the bridge hydrogens move 0.120 Å away from the plane formed by the three boron atoms, approximately preserving the B–H_b distances. This pronounced relative "skewing" of the MBPT(2) and SCF A_1 potential surfaces is one of the most striking correlation effects yet observed. A plausible explanation for this phenomenon is that the excited determinants mixed into the correlated molecular wave function act to increase electron density between the boron atoms, resulting in the observed shortening. Some support for this hypothesis comes from SCF and MBPT(2) studies of B_2H_6[4] and of BeB_2H_8,[6] in which correlation effects acted to stiffen the $B\cdots B$ (and $B\cdots Be$) harmonic force constants and slightly shorten the corresponding internuclear distances. In addition, Taylor and Hall showed that introduction of electron correlation had subtle but observable effects on the electron distribution in diborane, redistributing density from the B–H bonds into the "nonbonding" $B\cdots B$ region.[17] In B_3H_9, where the geometrical effect of correlation is an order of magnitude greater than in B_2H_6, it is possible that more substantial changes in the density occur. Our explanation is highly speculative, however, and will be subjected to careful examination through correlated calculations of the harmonic force field and electron density in B_3H_9.

Calculated electronic reaction energies for steps 1 and 2 of the B_2H_6 pyrolysis reaction are presented in Table II. In both cases, SCF and correlated results differ by approximately 20 kcal/mol. Augmentation of the basis form (321/21) to (431/31) has little

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Table III. Electronic and Vibrational Contributions to ΔE for the Reaction $BH_3 + B_2H_6 \rightarrow B_3H_9$, as Well as Enthalpy, Entropy, and Free Energy Differences Evaluated at 298 K (kcal/mol).

	(321/21)	(431/31)		(321/21)	(431/31)
ΔE_e	-9.3^a	-7.9^b	$T\Delta S°$	-9.9	-9.9
$\Delta E_0{}^c$	-5.3	-3.9	$\Delta G°$	3.4	4.8
$\Delta H°$	-6.5	-5.1			

[a] Calculated from the CCSD+T(CCSD) electronic energies. [b] Calculated from the MBPT(4) electronic energies. [c] $\Delta E_0 - \Delta E_e$ calculated from the (321/2) SCF frequencies scaled by a factor of 0.9.

Table IV. Symmetries and Harmonic Vibrational Frequencies (in Wavenumbers) for the Normal Modes of Borane(3), Diborane(6), and Triborane(9) Calculated at the SCF Level with the (321/2) Basis Set

BH_3		B_2H_6		B_3H_9	
sym	ω	sym	ω	sym	ω
A_1'	2641	A_g	2715	A_1	2834
A_2''	1206		2233		2702
E'	2779		1273		1753
E''	1268		817		1244
					1103
		A_u	882		534
					355
		B_{1g}	1869		
			888	A_2	2274
					989
		B_{1u}	2815		835
			1083		
			395	E	2820
					2689
		B_{2g}	2803		2249
			981		1798
					1218
		B_{2u}	2022		1169
			1058		957
					870
		B_{3g}	1166		569
					218
		B_{3u}	2694		
			1763		
			1252		

effect on the relative energies of B_2H_6 and BH_3 but favors the reactants in step 2 by about 2 kcal/mol at all levels of theory. Consistent with other studies of the dissociation of diborane[4,18,19] and analyses of the isomers of BeB_2H_8[6] and B_2H_4,[5] energy differences calculated with the economical MBPT(2) model are in good agreement with the highly correlated results. Also encouraging is the close correspondence between the SDQ-MBPT(4) (fourth-order MBPT excluding triple excitations) and MBPT(4) reaction energies and their more highly correlated CCSD and CCSD+T(CCSD) counterparts. This suggests that the correlation contribution to the reaction energy has nearly converged at the MBPT(4) level. In our calculations, the largest source of uncertainty is the finite size of the basis set. Experience has shown that associated errors are likely to be less than 5 kcal/mol.[20-22] Note that the common practice of using optimized SCF structures to compute reaction energies leads to an error of nearly 2 kcal/mol for reaction 2 (see Table II), while the approximation is excellent for the symmetric dissociation of diborane. Of course, this error is principally due to the large differences between the SCF and MBPT(2) structures of B_3H_9.

Zero-point and thermal corrections to the thermodynamic parameters for reaction 2 are documented in Table III; corresponding values for (1) have been presented elsewhere.[4] The vibrational corrections were calculated from the (321/2)-SCF harmonic frequencies listed in Table IV, scaled by a factor of 0.9. This scaling accounts, in an approximate way, for differences between harmonic and fundamental vibrational frequencies as well as inadequacies in the theoretical force field. Rotational contributions to the entropy and heat capacity were based on the (321/21)-MBPT(2) structural parameters. The dramatic shortening of the B···B distances at the MBPT(2) level leads us to believe that the zero-point correction of 4.0 kcal/mol is slightly underestimated, since it is logical to assume that correlation will act to increase the frequencies of many of the skeletal modes of this molecule.

Although B_3H_9 is favored relative to B_2H_6 and BH_3 at low temperatures, the substantial entropic contribution to the Gibbs free energy reverses this trend at room temperature. Consequently, it is unlikely that B_3H_9 serves to "trap" free BH_3 in diborane pyrolysis, which is typically carried out at temperatures near 400 K.[2] Our calculations suggest but do not prove that B_3H_9 is less stable than B_2H_6 and BH_3 under the reaction conditions but do offer convincing evidence that it is thermodynamically competitive, at best.

Summary and Conclusions

We have demonstrated that electron correlation has a dramatic effect on the ground-state structure of triborane(9), a crucial species in the commonly accepted mechanism for the pyrolysis of diborane, and we have presented theoretically determined reaction energies for the first two steps of the reaction process. The present results serve a valuable purpose by alerting us to the surprisingly poor picture of B_3H_9 provided by the independent electron approximation. Since reactions 2 and 3 involve bond breaking on the generalized B_3H_9 potential surface, it is almost certain that the single Slater-determinant description will be even more inadequate for the associated transition structures.[24] Thus, if our ongoing study of the pyrolysis mechanism is to have any meaning, full geometry optimization of the two transition states must be carried out at the correlated level. Furthermore, calculations by McKee and Lipscomb[23] suggest that d polarization functions on the boron atoms are necessary, as well. Using the valence double-ζ 3-21G basis, they found that the MBPT(2) B···B bond length in B_3H_9 was 2.10 Å, significantly longer than when polarization functions are included. The need for the more diffuse d functions makes physical sense, since these are needed to describe the interactions between the rather distant boron atoms. We are encouraged by the small differences between the geometries obtained with and without the large number (27) of polarization functions on hydrogen. This result suggests that MBPT(2) calculations using the (321/2) basis set may represent the minimum acceptable level for our transition-state searches. Results will be reported in a subsequent publication.

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Registry No. B_3H_9, 36350-66-0.

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