

The role of theory in studies of the diborane pyrolysis sequence

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Abstract - Theoretical studies to 4th order, or at coupled cluster levels using large basis sets have yielded a transition state for the reaction of BH_3 with B_2H_6 . This state is about 20 kcal/mole less stable than B_3H_9 (C_{3v}) and some 8 or 12 kcal/mole higher than H_2 plus B_3H_7 of symmetry C_{2v} or C_s , respectively. Therefore, most probably, $\text{B}_2\text{H}_6 + \text{BH}_3$ yields $\text{B}_3\text{H}_7 + \text{H}_2$ directly.

Neither B_3H_9 (C_{3v}) nor BH_5 trap BH_3 in usual pyrolysis conditions, and B_2H_6 to B_2H_4 and H_2 has a higher barrier. A different BH_3 adduct to B_2H_6 , forming a three-center bond between B of BH_3 and H (terminal) of B_2H_6 , has ΔE_e (electronic) of -1.5 kcal/mole at the (531/31)MBPT(2) level. This intermediate, suggested by Fehlner, needs further study.

As advances in theoretical studies of structures, transition states and reaction pathways occur, it is useful to reexamine especially the simpler, prototype of reactions. The pyrolysis of diborane, perhaps the oldest known reaction among boranes, is especially interesting as an example in which theoretical studies may contribute.

Experimental works [1, 2] have established the $\frac{3}{2}$ power dependence on pressure in the pyrolysis reaction, and have been followed by more detailed kinetic studies [3-6], which also include effects of inhibition of this reaction by H_2 . The sequence usually accepted is as follows



where reaction (3) is regarded as the rate determining step [3] in view of a large reported deuterium isotope effect ($k_H/k_D \approx 5$).

When adequate basis sets and correlation corrections are included in molecular orbital studies, many authors find no intermediate transition state for reaction (1), the dissociation of diborane. At the CCSD+T(CCSD) level of coupled cluster theory and with a 6-311G** (6d) basis set, ΔE_e (electronic) is 41.8 kcal/mole, ΔE_0 (zero-point corrected) is 35.2 kcal/mole and $\Delta H(360\text{K})$ is 37.4 kcal/mole [7].

Also, there is no intermediate barrier for reaction (3), which yields H_2 and the metastable C_{2v} , 1103 structure [8] (this vacant orbital structure is less stable by 4.2 kcal/mole than the 2102 isomer of C_s symmetry at the CCSD+T(CCSD) level using a [4s3p1d]/[3s1p] basis). Although a transition state was found, and was optimized at the MBPT(2) level using a [3s2p1d]/[2s1p] basis, the addition of polarization functions on hydrogen caused the optimization to fail, and further analysis indicated that this apparent barrier was spurious.

On the other hand reaction (2) does show a barrier of 13.6 kcal/mole at the MBPT(4) level and of 13.8 kcal/mole at the CCSD+T(CCSD) level using a [4s3p1d]/[3s1p] basis. The saddle point on the 30 parameter potential energy surface was optimized at the [3s2p1d]/[2s1p]-MBPT(2) level. The structure, which has C_1 symmetry (see Fig. 1), was obtained in part by use of chemical intuition, and resembles a protonated hydroboration reaction.

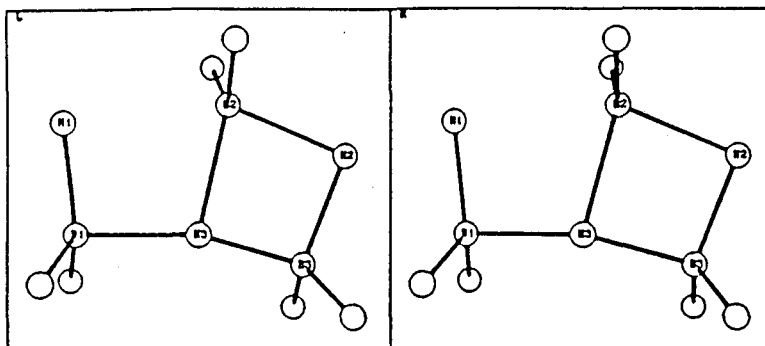


Fig. 1. Transition state for the reaction of BH_3 with B_2H_6 (TS 2), at the (321/21)-MBPT(2) saddle point.

Clearly, then, reaction (2) is rate limiting by these results. A closer analysis does not change this conclusion but indicates a different view of the whole sequence. What is the role of "stable" B_3H_9 of C_{3v} symmetry in these reactions? The ΔE_e is -7.5 kcal/mole for reaction (2) at the [4s3p1d]/[3s1p] CCSD+T(CCSD) level. However, the transition state for reaction (2) lies about 20 kcal/mole above the ground state for the C_{3v} structure of B_3H_9 , and about 8-12 kcal/mole higher than the products of reaction (3) depending on whether B_3H_7 has C_{2v} or C_s symmetry. Hence, the energies ΔE_e are highly suggestive of the *direct* reaction



provided only that collisional deactivation of the energetic B_3H_9 transition state is slow compared with loss of molecular hydrogen. A test of this proposal could be made if the reaction is carried out in the presence of a high pressure of inert molecules. We note that reaction (4) is also consistent with the $\frac{3}{2}$ power dependence on the pressure of diborane, and with hydrogen inhibition.

Because only the reaction of B_2H_6 and BH_3 has an intermediate barrier, the thermodynamics also is interesting. For example, it might appear from the ΔE_e values that B_3H_9 "traps" BH_3 as a stable intermediate, but this is not the case when the free energies are computed. Although ΔE_e is -7.5 kcal/mole for reaction (2) to B_3H_9 of C_{3v} symmetry, the Gibbs free energy change at 400 K is 8.7 kcal/mole. (The activation values are 13.8 kcal/mole for ΔE_e^\ddagger and 25 kcal/mole for $\Delta G^\ddagger(400K)$). Similarly, for reaction (3) to B_3H_7 of C_{2v} symmetry, ΔE_e is 13.5 kcal/mole, but $\Delta G(400K)$ is a favorable -2.4 kcal/mole. For the conversion of B_3H_7 from C_{2v} to C_s , there is no change in the number of molecules in the reaction so that ΔE_e is -4.2 kcal/mole and $\Delta G(400K)$ is -4.2 kcal/mole. Thus reaction (4) can proceed without trapping of BH_3 as stable B_3H_9 (C_{3v}).

In disagreement with the experimental [3] deuterium isotope effect of k_H/k_D of about 5 at 361 K, we find that at 400 K k_H/k_D is 1.7 if II is rate limiting or 2.4 if III is rate limiting [8]. These theoretical values are not significantly different from one another and therefore are not useful for distinguishing between reactions (2) and (3), but they are significantly lower than the experimental value. In a new experimental study [9], stimulated by our theoretical results, a value of k_H/k_D of 2.57 ± 0.65 at 420 K has been established. In view of uncertainties in the theoretical values we regard either as in satisfactory agreement with these new experimental results. Also, the theoretical values of K_H/K_D for reaction (1) suggest that B_2H_6 is dissociated to a greater extent than B_2D_6 at about 400 K (Fig. 2), in contradiction to an earlier prediction [4].

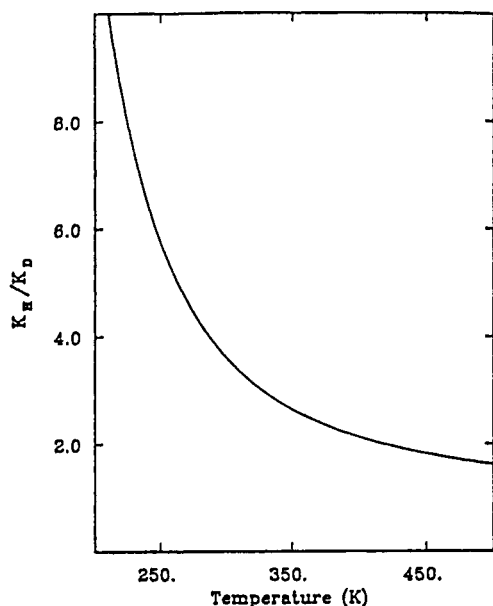


Fig. 2. Ratio of equilibrium constants for the unimolecular dissociation of $^{11}B_2H_6$ (K_H) and $^{11}B_2D_6$ (K_D).

A detailed theoretical study [10] of BH_5 at the CCSD+T(CCSD) level using a large [5s4p3d1f]/[4s2p1d] basis indicates that, for the dissociation reaction to BH_3 and H_2 , ΔE_e is 5.4 kcal/mole and $\Delta G(298K)$ is -4.1 kcal/mole. The results are strongly dependent on basis sets. Although the complex is predicted to be unbound with a split-valence [3s2p]/[2s] basis, introduction of polarization functions results in a stable BH_5 minimum. Binding energies are 2.7 kcal/mole for a singly polarized [3s2p1d]/[2s1p] basis, as compared with the 5.4 kcal/mole above. The unfavorable free energy of association (4.1 kcal/mole) corresponds to an equilibrium constant of about 10^{-3} M, and indicates that under the usual pyrolysis conditions BH_3 in the presence of hydrogen is not trapped appreciably as BH_5 . Internal rearrangement of H atoms in BH_5 is predicted to have an enthalpic barrier of 6.6 kcal/mole [10].

An unexpected effect of electron correlation on predicted molecular geometries was found for the transition state of the $B_2H_6 + BH_3$ reaction and for the equilibrium C_{3v} structure for B_3H_9 [11]. For example, the nominally non-bonded B...B distance in B_3H_9 is shortened from 2.168 Å in the SCF [3s2p1d]/[2s1p] basis to 2.018 Å with the same basis at the MBPT(2) level. This effect of electron correlation in increasing the bonding density between boron atoms may require some new aspects which modify slightly the usual description of chemical bonds in these molecules.

The proposal that the formation of B_2H_4 and H_2 from B_2H_6 is involved in the pyrolysis of diborane, as discussed by Massey [12], has been shown to be unlikely; this reaction has a significant barrier (although a reasonable zero-point dissociation energy of 36.7 kcal/mole) as compared with the zero intermediate barrier for dissociation of B_2H_6 to two BH_3 molecules. The structures of B_2H_4 have been investigated [13] at the 6-31G*-MBPT(2) level, at which the D_{2d} (0012) and C_{2v} (2010) have nearly the same energies. The geometries are shown in Fig. 3 as I and II, respectively, where the bridge hydrogens are the usual three center, two electron bonds.



Fig. 3. Structures of approximately equal energies for B_2H_4 .

At the 6-31G*-MBPT(2) level I is more stable than II by only 1.5 kcal/mole [13], while at the CCSD+T(CCSD) level using a 6-311G**(6d) basis set we find again that I is more stable than II, by only 1.3 kcal/mole for ΔE_e and 2.1 kcal/mole for ΔE_o (zero-point corrected) [14].

A very recent theoretical study by Curtiss and Pople includes further corrections to the basis sets and correlation, and indicates preferred stability of II over I by only 0.1 kcal/mole [14]. Preparation of B_2H_4 and a study of photoionization mass spectra has also very recently appeared [16], and supports the approximately 1:1 ratio of structures I and II for B_2H_4 . These two structures indicate the delicate balance here between strain, which favors I over II, and correlation stabilization which favors conversion of terminal hydrogen to bridge hydrogen when a vacant orbital on boron is available thus favoring II over I.

Quantum mechanical tunneling can be expected to play some role especially when motions of hydrogen atoms are important when the complex is near the top of an intermediate barrier on the potential energy surface. For example, in the hydrogen scrambling reaction in BH_5 [10] we have applied Miller's modified RRKM model [17-19] which includes an approximate treatment of quantum effects. In this example, a significant rate ($> 10^6 s^{-1}$) persists at an energy which is 5 kcal/mole below the classical threshold. More sophisticated models which do allow coupling of the reaction coordinate with the remaining 3N-7 vibrational modes are advised [20]. Tunneling may also account for part of the remaining discrepancy of about (3.8=13.8-10) kcal/mole in the kinetics of the reaction sequence (1), (2) and (4) for the initial stages of diborane pyrolysis. Also, other improvements, e.g. in basis sets and correlation, may remove some of this remaining discrepancy.

A final aspect of the reaction of B_2H_6 with BH_3 relates to the direct observation of a B_3H_x species [21]. Our predicted rate constant for formation of B_3H_9 is about 10^7 smaller than that measured for direct formation of this B_3H_x . Fehlners comments [22] that this B_3H_x may be a weak complex of BH_3 and B_2H_6 which may or may not rearrange to the transition state of Fig. 1, and that the rate constant of $10^6 M^{-1}s^{-1}$ for its formation from BH_3 and B_2H_6 suggests an effective "barrier" (including orientation effects) of about 7 kcal/mole or less, while a barrier to further rearrangement must be about 9 kcal/mole or more in order to permit its observation.

We therefore have explored an adduct of the form suggested by Fehlners: approach of a BH_3 so that the vacant orbital on B makes a three center bond with one terminal hydrogen of B_2H_6 . The geometry was optimized at the MBPT(2) level with the [3s2p1d]/[2s1p] basis, and final energy calculations were made at the MBPT(2) level using the [3s2p1d]/[2s1p] and [5s3p1d]/[3s1p] basis sets and the frozen core approximation. The ΔE_e is -1.5 kcal/mole for formation of the adduct using the (531/31) MBPT(2) results. Further work is required at higher levels of basis sets and correlation to see if sufficient binding develops to overcome the unfavorable entropy of association of two molecules to form one. This adduct, or a similar one obtained by bridging more than one hydrogen atom may be involved in exchange between B_2H_6 and B_2D_6 as observed by Maybury and Koski [23].

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REFERENCES

- [1] R.P. Clarke and R.N. Pease *J. Am. Chem. Soc.* 73, 2132-2134 (1951).
- [2] J.K. Bragg, L.V. McCarty and F.J. Norton *J. Am. Chem. Soc.* 73, 2134-2140 (1951).
- [3] R.E. Enrione and R. Schaeffer *Inorg. Nucl. Chem.* 18, 103-107 (1961).
- [4] G.L. Brennan and R. Schaeffer *Inorg. Nucl. Chem.* 20, 205-210 (1961).
- [5] T.P. Fehlners, in *Boron Hydride Chemistry*; E.L. Muettterties, ed., (Academic Press, New York, 1975), pp. 175-196.

- [6] N.N. Greenwood and R. Greatrex *Pure Appl. Chem.* 59, 857-868 (1987).
- [7] J.F. Stanton, R.J. Bartlett and W.N. Lipscomb, in *Molecules in Physics, Chemistry and Biology, Vol. III*; J. Mauriani, ed., (Kluwer Academic Publishers, 1988), pp. 357-363.
- [8] J.F. Stanton, W.N. Lipscomb and R.J. Bartlett *J. Am. Chem. Soc.* 111, 5173-5180 (1989).
- [9] R. Greatrex, N.N. Greenwood and S.M. Lucas *J. Am. Chem. Soc.* 111, 8721-8722 (1989).
- [10] J.F. Stanton, W.N. Lipscomb and R.J. Bartlett *J. Am. Chem. Soc.* 111, 5163-5173 (1989).
- [11] J.F. Stanton, W.N. Lipscomb, R.J. Bartlett and M.L. McKee *Inorg. Chem.* 28, 109-111 (1987).
- [12] A.G. Massey *Chem. Br.* 16, 588-598 (1980) and references therein.
- [13] R.R. Mohr and W.N. Lipscomb *Inorg. Chem.* 25, 1053-1057 (1986).
- [14] J.F. Stanton, W.N. Lipscomb and R.J. Bartlett *Proc. 6th International Meeting on Boron Chemistry*, S. Hermanek, ed., (World Scientific, Teaneck, 1987), pp. 78-82.
- [15] L.A. Curtis and J.A. Pople *J. Chem. Phys.* 91, 5118-5119 (1989).
- [16] B. Ruscic, M. Schwarz and J. Berkowitz *J. Chem. Phys.* 4576-4581 (1989).
- [17] W.H. Miller *J. Am. Chem. Soc.* 101, 6810-6814 (1979).
- [18] B.C. Garrett and D.G. Truhlar *J. Phys. Chem.* 83, 1079-1112 (1979).
- [19] W.H. Miller *Accounts Chem. Res.* 9, 306-312 (1976).
- [20] W.H. Miller, N.C. Handy and J.E. Adams *J. Chem. Phys.* 72, 99-110 (1980).
- [21] S.A. Fridmann and T.P. Fehlner *Inorg. Chem.* 11, 936-940 (1972).
- [22] T.P. Fehlner, private communication.
- [23] W.S. Koski and P.C. Mayberry *J. Chem. Phys.* 21, 742-747 (1953).