

ELECTRON CORRELATION EFFECTS IN BORON HYDRIDE STRUCTURES, INTERMEDIATES AND REACTIONS

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Abstract - Electron correlation effects are required in order to obtain reliable theoretical estimates of the transient stability of BH_5 , the dissociation energy of diborane, and the choice of most stable geometries for B_2H_7 , B_3H_7 , B_4H_8 , B_4H_{10} and B_5H_{11} . A progress report shows that the 2-2, 2-3, and 3-3 bridged structures for $Be(BH_4)_2$, where $BBeB$ is assumed linear, have nearly equal energies, although studies of the bent forms are incomplete. Reactions such as $BH_3 + B_2H_6 \rightarrow B_3H_9$, $B_3H_9 \rightarrow B_3H_7 + H_2$, $2B_2H_6 \rightarrow BH_3 + B_3H_9$, and $B_4H_8 + B_5H_{11} \rightarrow B_4H_{10} + B_5H_9$ are also discussed.

INTRODUCTION

The polymerization of diborane to higher hydrides, discovered by Stock (Ref. 1), is not well understood. Even the dependence of the initial rate on the $3/2$ power of the pressure has been interpreted in terms of dissociation of B_2H_6 into $2BH_3$ (Ref. 2 & 3), or reaction of two B_2H_6 to give $BH_3 + B_3H_9$ (Ref. 4). If the former reaction is correct, it is not yet clear whether the reaction of BH_3 with B_2H_6 to give B_3H_9 , or the loss of H_2 from B_3H_9 is rate limiting (Ref. 5).

Methods

The occasion for this study is the recent discovery of a theoretical method for obtaining reasonably accurate energies for reactions or isomerizations (Ref. 6). We have found that for simple reactions, such as those not involving unpairing of electrons, the corrections to the self-consistent field (SCF) level for polarization and correlation are additive, and that they give reaction energies to within a few to several kcal/mole. In practice, the geometries are usually optimized at the 3-21G SCF level (3 Gaussian atomic orbitals for 1s, two for 2s and 2p with one exponent, and one for 2s and 2p with another exponent), and the initial wave-function is computed at the 6-31G SCF level. The correction for polarization

$$\Delta_{pol} = (6-31G^{**} - 6-31G)_B - (6-31G^{**} - 6-31G)_A \quad (1)$$

includes d orbitals on the first row element (first *) and p orbitals on hydrogen (second *), for products B and reactants A. The electron correlation corrections were made by including all double excitations (Ref. 7 & 8) (CID level) or by Møller-Plesset perturbation corrections of the SCF wave-function to second order (MP-2) or third order (MP-3). Specifically for CID corrections

$$\Delta_{CI} = (CID/6-31G - 6-31G)_B - (CID/6-31G - 6-31G)_A \quad (2)$$

where, as before, energies are entered into the equation at the indicated level of approximation.

Now, if both polarization and correlation corrections were made, we would have

$$\Delta_{pol} + CI = (CID/6-31G^{**} - 6-31G)_B - (CID/6-31G^{**} - 6-31G)_A \quad (3)$$

Unfortunately, this is an impossibly large calculation for systems having more than about three boron atoms. However, for these and smaller systems we have found, to a good approximation that

$$\Delta_{\text{pol}} + \text{CI} \sim \Delta_{\text{pol}} + \Delta_{\text{CI}} \quad (4)$$

I emphasize that this approximate equality holds for an equation or isomerization, and is not valid for A or B alone. Thus, it depends upon an approximate cancellation of effects of excitations from the added polarization orbitals. Probably then, the method will fail if the d orbitals on the first row element, or the p orbitals on hydrogen are appreciably occupied. Hence, revisions may be required for elements further down the periodic table. Open shells probably will also present a problem. Our use here for some transition states may, however, require larger basis sets and more extensive CI corrections than ground states.

The desirability of geometry optimization using large (6-31G*) basis sets and including electron correlation at the MP-3 or CID level has recently been exemplified by Pople and coworkers (Ref. 9). They studied all experimentally determined neutral molecules of up to two first row elements bound to any number of hydrogen atoms. The majority of bond distances and angles are predicted within experimental error at these levels, although predicted distances are too long at the MP2/6-31G* level, and too short at the 6-31G* level. Much of the recent literature on effect of electron correlation in theoretical studies of molecular geometry is summarized in this reference.

For larger molecules, such as most of those discussed below, less complete methods must be used in view of the computational effort required. Geometries are reasonably well predicted for the more familiar organic molecules even at the STO-3G or STO-4G level if exponents of the valence shell are optimized (Ref. 10). (Here, three or four Gaussian functions are used for each Slater-type orbital.) However, for those boron hydride species in which tautomeric transformations of a bridge hydrogen to a terminal hydrogen occur along with compensating changes in bonding among the framework orbitals, electron correlation corrections become important. These corrections are not appropriate unless a larger basis set, approximately 6-31G*, is employed. A major reason is that the two electrons in a terminal BH bond encounter one another more readily than do the two electrons in a three-center BHB bridge. The transformation of a central BBB three-center bond to a BB single bond requires a similar, but smaller, correlation correction.

RESULTS

BH₅. This molecule is a transient intermediate (Ref. 11 & 12) in the reaction of BH₄⁻ with H⁺. Its structure (Fig. 1) is similar to that of CH₅⁺ which is a weak adduct of CH₃⁺ to H₂ (Ref. 13).

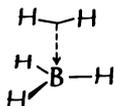


Fig. 1. Structure of BH₅, a weak adduct of BH₃ to H₂.

The H₂ and BH₃ are unbound at the SCF level, and when correlation corrections are included BH₅ is more stable than H₂ + BH₃ by about 2kcal/mole (Ref. 6, 14-16).

B₂H₆. The SCF limit for a large basis set is about 19 kcal/mole (Ref. 17) for the dissociation energy of B₂H₆ into 2BH₃ molecules. Inasmuch as the observed ΔH of dissociation is 35.5 kcal/mole (Ref. 18) the correction for electron correlation is very large. The additivity method described above gives a dissociation energy of 35.6 kcal/mole (Ref. 6) in agreement with an early value of 36.6 kcal/mole (Ref. 19) and with a value of 35.6 kcal/mole (Ref. 20) obtained by many body perturbation theory. Thus correlation effects, primarily associated with conversion of two terminal hydrogens, account for almost half of the dissociation energy of diborane (Fig. 2).



Fig. 2. Structure of B₂H₆. A bridge hydrogen is represented by a curved line, and a terminal hydrogen is indicated by a straight line.

B_3H_7 . Prepared by pyrolysis (Ref. 21) of $(CH_3)_2NF_2PB_3H_7$, the B_3H_7 molecule is at best a transient intermediate in the pyrolysis of B_2H_6 to yield higher hydrides. Perhaps a spectroscopic study of its structural properties would be feasible by matrix isolation techniques. The structures of adducts, $B_3H_7NH_3$ (Ref. 22 & 23) and B_3H_7CO (Ref. 24) show only one bridge hydrogen. However, the structure of the B_3H_7 moiety is surely influenced by the B-N or B-C bond in these adducts. The additivity method (Ref. 6) for polarization and correlation corrections predicts that the 2102 structure (Fig. 3a) is more stable than the 1103 structure (Fig. 3b) by only 4.4 kcal/mole (Ref. 25). The same method indicates that the 2012 structure

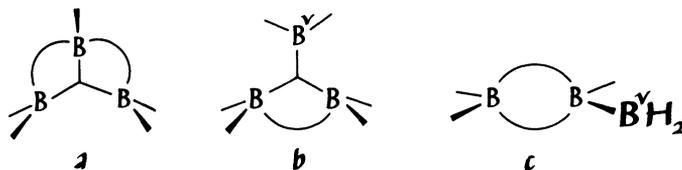


Fig 3. Structures for B_3H_7 . (a) 2102, (b) 1103 and (c) 2012. The symbol v denotes a vacant orbital. The four numbers refer, in order, to s the number of bridge hydrogens, t the number of BBB three-center bonds, y the number of BB single bonds and x the number of terminal hydrogens in excess of one.

(Fig. 3c) is only 7.4 kcal/mole less stable than the 2102 structure. While additional correlation corrections may further enhance the relative stability of the 2102 structure, it seems likely that the structure is fluxional between 2102 and 1103.

$B_3H_8^-$. The fluxional nature of $B_3H_8^-$, including both pseudorotation and BH_3 rotation, was first inferred from the ^{11}B spectrum (Ref. 26). The limiting structures (Fig. 4), of 2013 and 1104 topologies, illustrate a transformation which makes all boron atoms equivalent and all hydrogen atoms equivalent on the nmr time scale. This fluxional character survives correlation corrections: the 2013 structure is only 0.8 kcal/mole more stable than the 1104 structure (Ref. 25) when the polarization and correlation corrections are added as described above. The single bond in the 2013 structure has some three-center character, which causes the two bridge hydrogen atoms to be displaced away from the boron atom at the top of Fig. 4a. In the crystalline phase, the 2013 structure has been found (Ref. 27).

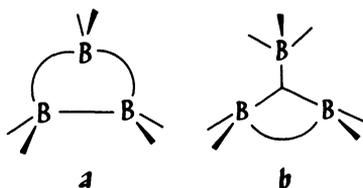


Fig. 4. Limiting structures for pseudorotation and BH_3 rotation in $B_3H_8^-$.

B_3H_9 . At the level of theory outlined above, including additive polarization and correlation corrections (MP3), B_3H_9 is 4.1 kcal/mole less stable (Ref. 28) than its probable precursors, B_2H_6 plus BH_3 . At the MP2 level, plus polarization, the value is similar, 3.8 kcal/mole, but at the 6-31G level without these polarization and correlation corrections B_3H_9 is less stable than these reactants by 13.3 kcal/mole. The assumed geometry (Fig. 5) has D_{3h} symmetry, and is of 3003 topology. The transition state between B_3H_9 and B_2H_6 plus BH_3 is discussed below.

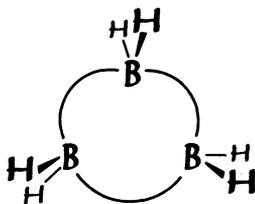


Fig. 5. Structure of B_3H_9 , of symmetry D_{3h} and topology 3003.

B_4H_8 . An "unusually stable" transient intermediate, B_4H_8 , has been prepared by pyrolysis (Ref. 29) of the stable adduct, B_4H_8CO . An X-ray diffraction study (Ref. 30) of $B_4H_8PF_2N(CH_3)_2$ yields the 2112 structure for the B_4H_8 moiety, shown in Fig. 6b. The vacant orbital of the 2112 structure can be partially filled by conversion of a BH terminal hydrogen to a bridge (Fig. 6a). Additivity of polarization and correlation (Ref. 28) favors the 3-bridged 3111 structure over the 2112 structure by 4.2 kcal/mole, and over the four-bridged 4020 structure of Fig. 6c by 5.7 kcal/mole. Perhaps the three-bridged structure is a compromise between strain and correlation stabilization, and probably the B_4H_8 molecule is fluxional.

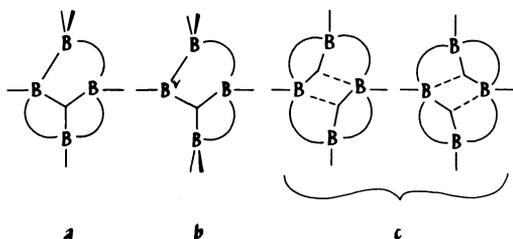


Fig. 6. Structure of B_4H_8 . (a) 3111(C_1), (b) 2112(C_s) as found in $B_4H_8PF_2N(CH_3)_2$, and (c) 4020(C_{2v}). The 4020 notation ignores fractionality of bonds in the resonance hybrid.

B_4H_{10} . It is remarkable the level of theory which is required to decide whether the observed structure (Ref. 31) of B_4H_{10} (Fig. 7a) is more stable than the bisdisborane ($B_2H_5-B_2H_5$) structure (Ref. 32) (Fig. 7b). Additivity of polarization and electron correlation shows that the observed structure is more stable than the gauche bisdisborane structure by only 2.7 kcal/mole (Ref. 33). The trans and cis diborane structures are less stable than the gauche isomer by 2 kcal/mole and 3.5 kcal/mole, respectively. Another study (Ref. 34) of the two

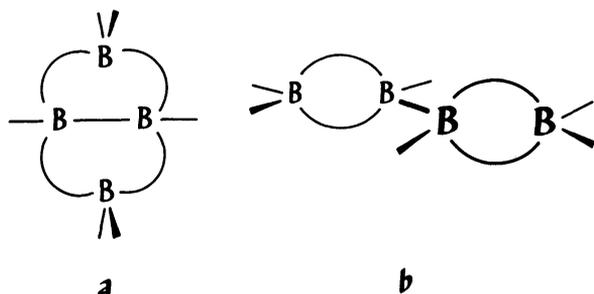


Fig. 7. Structures for B_4H_{10} (4012); (a) observed, (b) the bisdisborane structure.

isomers, including some configuration interaction yields the result that the observed structure approaches that of the trans bisdisborane structure, and it is extrapolated that the observed structure would be predicted to be more stable in a treatment of electron correlation beyond this generalized molecular orbital approach (Ref. 34).

B_5H_{11} . Although the early X-ray diffraction study (Ref. 35) assigned C_s symmetry to B_5H_{11} , it was recognized that the atomic coordinates, particularly those of hydrogen, were not well established. The nmr study (Ref. 36) did not allow a choice among a C_s structure (in which the extra hydrogen atom on the apex boron was symmetrical and partially bridged), a slightly distorted C_1 structure, or two equivalent rapidly interconverting C_1 structures. An accurate X-ray diffraction study (Ref. 37) has established molecular symmetry C_1 (Fig. 8a), although it was not certain whether the small distortions from C_s symmetry (Fig. 8b) were associated

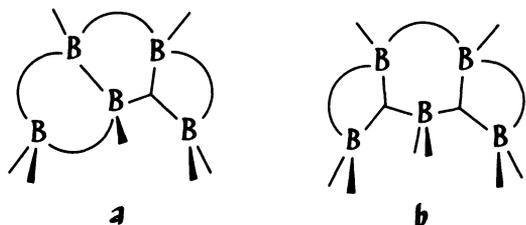


Fig. 8. Structures for B_5H_{11} . (a) 4112(C_1), (b) 3202(C_s).

with intermolecular packing. We find that additivity of the polarization correction (6-31G*) and the correlation correction (MP-2) to the 6-31G wavefunction predicts that the C_1 structure is more stable than the C_s structure by only 1.7 kcal/mole (Ref. 38). Possibly the inclusion of polarization functions on hydrogen and a higher level of correlation correction would further stabilize the C_1 structure relative to the C_s structure. However, it is likely that theory would still predict that the molecule is fluxional.

PROGRESS REPORTS

$B_2H_7^-$. At the SCF minimum basis level $B_2H_7^-$ has been predicted (Ref. 17) to have a linear BH_bB configuration (Fig. 9). However, recent calculations on the isoelectronic $C_2H_7^+$ ion predict a bent CH_bC arrangement (Ref. 39 & 40). A recent crystal structure study (Ref. 41) indicates a bent structure for $B_2H_7^-$ in which BH_bB is about 136° and $B\dots B$ is 2.107 Å. The hydrogen bridge is asymmetric such that BH_b is 1.27 Å and 1.00 Å on the two sides of H_b . A reinvestigation of the theoretical structure is in progress (Ref. 42), in which additivity of both polarization (6-31G**) and correlation (MP-3) corrections to the 6-31G level has been made. These calculations predict a stability of 0.28 kcal/mole for a bent ($BH_bB=112.4^\circ$) structure ($B\dots B$ constrained at 2.107 Å) over the very slightly bent ($BH_bB = 172.0^\circ$) structure ($B\dots B$ optimized: 2.65 Å). The $B\dots B$ distance and all other geometrical parameters in both structures were optimized at the 3-31G level, and in both structures the hydrogen bridge is symmetric. For the bent structure at the MP3/6-31G** additivity level, the calculated ΔE_f for the reaction $BH_3 + BH_4^- \rightarrow B_2H_7^-$ is -33.7 kcal/mole, in agreement with the experimental ΔH_f of -31.0 ± 8 kcal/mole (Ref. 43). In the full calculation at the MP3/6-31G** level, the bent structure is more stable than the near-linear structure by 0.35 kcal/mole, and the ΔE for $BH_3 + BH_4^- \rightarrow B_2H_7^-$ is -36.5 kcal/mole.



Fig. 9. Structure for $B_2H_7^-$. (a) linear BH_bB , (b) bent BH_bB .

$Be(BH_4)_2$. Only three structures, of nine candidates, appear so far to be most stable in SCF calculations at or near the minimum basis set level for $Be(BH_4)_2$ (Ref. 44 & 45):

$H_2BH_2BeH_2BH_2(2,2)$, $H_2BH_2BeH_3BH(2,3)$ and $HBH_3BeH_3BH(3,3)$ where the symbols in parenthesis refer to the numbers of hydrogen bridges (Fig. 10). In these calculations the (2,2) structure is more stable than (2,3) by 6.5 kcal/mole, and more stable than (3,3) by 7.3 kcal/mole. This

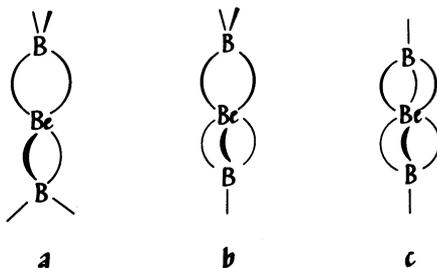


Fig. 10. Structures for $Be(BH_4)_2$. (a) (2,2), (b) (2,3) and (c) (3,3), where the descriptions here refer to the numbers of hydrogen bridges.

ordering persists as the basis set is extended to 6-31G**, but when many body perturbation theory is employed to third order these three isomers are at relative energies of 0(2,2), 2.2(2,3) and 0.6(3,3) in kcal/mole (Ref. 46). Thus correlation corrections reduce the differences in relative energies of these three isomers. The conclusion so far, that the molecule is fluxional with a linear $BBeB$ arrangement, needs further study in view of the dipole

moment of 2.1 debyes (Ref. 47) for at least part of the molecules in the gas phase, and in view of the complexities of the infrared and Raman spectra (Ref. 48) and of the various electron diffraction patterns. The (2,3) structure has a calculated dipole moment of only 0.9 debyes at the 6-31G** level (Ref. 46). Release of geometrical symmetry constraints on the (2,3) structure in further optimization gives rise to a structure that strongly resembles the (3,3) geometry, before the slowly converging optimization was terminated. It was clear that the (3,3) structure would be found at the energy minimum at this stage. Slight variations from linearity of B-Be-B in the (3,3) structure gave rise to a (2,3) structure. Our calculations at the 4-31G level indicate that the relative stabilities of the (3,3) and (2,3) structures are very sensitive to the B-Be-B angle in the vicinity of 180°. Further theoretical studies of this distortion would be desirable.

B₃H₉ transition state (B₂H₆ + BH₃). Of the several ways in which BH₃ can approach B₂H₆, we have been guided by the model in which both donation and back-donation of electrons occurs (Ref. 49). Because of the very large number of parameters (Fig. 11) a series of constrained geometry optimization was carried out at the 3-21G level, in which various fixed distances were assigned to the two designated distances in Fig. 11. (A suitable reaction coordinate is the ratio of these two distances.) A partial further optimization, excluding variation of terminal hydrogen parameters and the two constrained hydrogens, was made at the MP-2/6-31G level. Using this geometry and the additivity of polarization (6-31G*) and electron correlation (MP-3) corrections to the 6-31G level, we find barriers of 22.4 kcal/mole for the formation of B₃H₉, and of 18.7 kcal/mole for the reverse reaction (Ref. 28). (B₃H₉ is calculated to be less stable than B₂H₆ plus BH₃ by 4 kcal/mole).

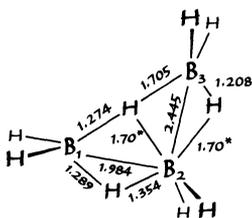


Fig. 11. Plausible transition state for the reaction of B₂H₆ with BH₃ to give B₃H₉. The distances denoted by an asterisk were held constant in the geometry optimization at the 3-21G level.

B₃H₉ transition state to B₃H₇ + H₂. No constraints were assumed. Here, a very short H...H distance occurs (Fig. 12). The very different geometry of this transition state as compared with that of Fig. 11 is consistent with calculations which indicate that the concerted transition state, in which H₂ is lost as BH₃ adds to B₂H₆, is much less stable. Here, the barrier for B₃H₉ decomposition is 12.6 kcal/mole, while that for the reverse reaction is about 18 kcal/mole, after additive corrections for polarization and electron correlation have been made (Ref. 28).

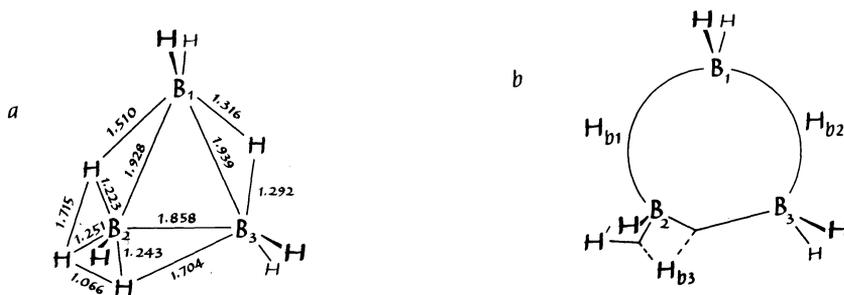


Fig. 12. Plausible transition state for loss of H₂ from B₃H₉. (a) Geometry; (b) Localized molecular orbitals.

DISCUSSION

The section on Results establishes the generality of the need for polarization and (especially) correlation corrections. Of course, the inconsistency of the theoretical procedures, in which some geometries had to be established without these corrections, is clear. However, as molecular orbital methods, including geometry optimization, develop further, these and other multiparameter optimizations will become feasible, and constraints can be removed.

Transition states, as contrasted with ground states of isomers, present a more severe problem to theory. Taken at face value the lower activation energy for disappearance of B_3H_9 to $B_3H_7 + H_2$ is favored over the formation of $BH_3 + B_2H_6$. Moreover, the rate determining step appears to be the formation of B_3H_9 , rather than its decomposition to $B_3H_7 + H_2$. However, all is not well with this interpretation. The experimental barrier is only about 27 kcal/mole, while the calculated barrier is 40 kcal/mole (35.5/2 kcal/mole from the B_2H_6 decomposition plus 22.4 kcal/mole for the formation of B_3H_9). It is unknown at this time whether the difficulties are due to inadequate theory, insufficient orbital basis sets, imprecise location of the transition state, a different mechanism, zero point corrections, or tunneling. At least, the large deuterium isotope effect (Ref. 50) on the early stages of polymerization of B_2H_6 indicates that both tunneling and the zero point corrections are important. Moreover, if the 22.4 kcal/barrier is to be reduced to about 10 kcal/mole by one or more of these effects, and if the barrier for decomposition to $B_3H_7 + H_2$ were to be much less affected (because of the product-like transition state) even the identification by theory of the early rate determining step is uncertain. Hence, for transition states there remains much to be learned by these purely theoretical methods.

The reaction energy calculations are more secure. They indicate that B_3H_9 is a bit less stable than $BH_3 + B_2H_6$, and thus do not favor, but do not eliminate, a mechanism such as that proposed by Long (Ref. 4) in which two B_2H_6 molecules form B_3H_9 and BH_3 . (However, our transition state for this latter reaction is energetically very unfavorable.) Perhaps the most interesting reaction from the viewpoint of energetics is



which is exothermic by 30 kcal/mole in our calculations. While this may not be the only pathway to B_5H_9 , it may be an important one. Of course, the activation energy of this reaction, as well as that for the formation of B_4H_8 from B_4H_{10} (24 kcal/mole)(Ref.51), will be significant in the rates. The required temperature is high enough that the B_4H_{10} would be decomposed to H_2 and B_4H_8 , so that B_4H_8 is essentially a catalyst for the loss of H_2 from B_5H_{11} in this proposed reaction.

Finally, a qualitative view of the transition state for the formation of B_3H_9 from B_2H_6 and BH_3 is that it is a protonated hydroboration reaction, in which the triply bridged proton is interacting with the approaching boron of BH_3 and with the (protonated) double bond of B_2H_6 . At the same time, one terminal BH of the BH_3 adds to one boron atom of the B_2H_6 . This may be a general feature of BH_3 addition reactions to BH_2B units in the higher hydrides.

APPENDIX

The decomposition of formaldehyde into carbon monoxide and hydrogen has become a test case for calculating a rate constant. While the theoretical effects found in this reaction are not directly applicable to the transition states discussed above, some essential results are as follows. (1) Neglect of polarization functions (p orbitals) on hydrogen leads to errors of up to 6 kcal/mole in the activation energies, and further neglect of d orbitals on first row atoms leads to additional error of up to 10 kcal/mole (Ref. 52). (2) The reduction of the barrier when zero point energies are taken into account is about 5 to 6 kcal/mole (Ref. 53). (3) Proton tunneling is important, and may be equivalent to reducing the calculated barrier by some 5-10 kcal/mole (Ref. 54 & 55). It is to be emphasized that this is a slow reaction, which has a barrier of about 87 kcal/mole.

ACKNOWLEDGEMENT

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