The AM1 and PM3 molecular orbital methods have been utilized to investigate the reactions of CH2OH with NO and NO2. PM3 and AM1 calculated heats of formation differ from experimental values by 8.6 and 18.8 kcal mol\(^{-1}\), respectively. The dominant reaction of CH2OH with NO is predicted to produce the adduct HOCH2NO, supporting the hypothesis of Pagsberg, Munk, Anastasi, and Simpson. Calculated activation energies for the NO2 system predict the formation of the adducts HOCH2NO and HOCH2ONO. In addition, the PM3 calculations predict that the abstraction reaction producing CH2O and HONO is more likely than one producing CH2O and HONO from reactions of CH2OH with NO2.

Introduction

The hydroxymethyl and methoxy radicals are important intermediates in the combustion of methanol.\(^{(1)}\) There have been many studies concerning the methoxy radical but relatively few on its isomer. Most of the previous studies of the hydroxymethyl radical, CH2OH, have concerned the kinetics of reactions involving O2.\(^{(2,3)}\) The ultraviolet absorption spectrum of CH2OH has been reported\(^{(4)}\) and used to monitor the kinetic behavior of this radical in reactions with O2, NO, and NO2 at room temperature and 1 atm pressure. The present work uses semiempirical molecular orbital methods to calculate the activation energy barriers and energetics for reactions of CH2OH with NO and NO2.

As for (DEE)\(^2\)H\(^+\)-DEE, even though the binding energy is not known, the value is expected to be much smaller than 1.2 eV due to the complete hydrogen-bonding solvation shell formation at (DEE)\(^2\)H\(^+\). The binding energy of cluster ion (C2H5OC2H5)\(^+\)-CH2OCH3 is measured to be 0.40 eV, and that of (C2H5OC2H5)\(^+\)-C2H5OC2H5 should be of comparable magnitude, which is smaller than the energy required for reaction 20. Our observation of C2H5OC2H5 loss for \(n = 3\) and C2H5OC2H5 loss for \(n = 4\) is consistent with these thermochemical values and the general expectation that the reaction pathways are based on the energetics.

IV. Conclusion

A number of chemical reactions take place upon multiphoton ionization of neutral dimethyl and diethyl ether clusters. Intramolecular proton-transfer reactions dominate in both cases, as evidenced by the fact that protonated cluster ions are the most abundant species. An intramolecular hydrogen-transfer reaction is responsible for the unique stability of unprotonated diethyl ether dimer ion. It is observed that the presence of water molecules greatly suppresses reactions leading to product (CH3OC2H5)\(^+\)+CH2OH, but formation of (C2H5OC2H5)\(^+\)+C2H5OH\(^-\) is not influenced. These findings can be understood on the basis of different reaction mechanisms.

Acknowledgment. Support by the U.S. Department of Energy, Grant No. DE-FGO2-88-ER60668, is gratefully acknowledged.
and NO$_2$.$^{12}$ The new parametrization used to generate the PM3 method$^{12'}$ has reduced the overall error between heats of formation for neutral radicals and neutral molecules even further. Extensive calculations of reactions of radicals have not yet been performed with the PM3 method. In this paper, results are compared with pulse radiolysis/kinetic analysis experiments$^{9}$ and other experimental values.

Pagsberg et al.$^{9}$ reacted CH$_2$OH with various target molecules and used the ultraviolet absorption spectrum of CH$_2$OH to monitor its decomposition. They proposed the following reaction mechanisms to account for the varying reactivity of CH$_2$OH with NO and NO$_2$:

\[
\begin{align*}
\text{CH}_2\text{OH} + \text{CH}_2\text{OH} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} + \text{NO} & \rightarrow \text{CH}_2\text{O} + \text{HNO}
\end{align*}
\]

In this work the following reactions have also been considered:

\[
\begin{align*}
\text{CH}_2\text{OH} + \text{NO} & \rightarrow \text{CH}_2\text{O} + \text{HNO} \\
\text{HONO} & \rightarrow \text{HOCH}_2\text{ONO} \\
\text{CH}_2\text{OH} + \text{NO}_2 & \rightarrow \text{CH}_2\text{O} + \text{HNO}_2
\end{align*}
\]

The goal of this work is to compare and contrast the experimental information with results of quantum mechanical calculations in order to gain further insight into reactions of CH$_2$OH with NO and NO$_2$.

Method

In this investigation the semiempirical molecular orbital programs developed by Dewar and co-workers$^{10-13}$ have been employed to calculate the products and transition-state structures for reactions of CH$_2$OH with NO and NO$_2$. MINDO/3, based on the INDO approximation, was the first truly successful semiempirical molecular orbital program.$^{10,14}$ In this quantum mechanical method, valence electrons are assumed to move in a fixed core of nuclei and inner-shell electrons and are treated by using a minimum basis set simplified by neglecting certain electron repulsion integrals involving differential overlap. The remaining integrals are then equated to functions containing numeric parameters that have been adjusted to fit experimental data. MINDO/3 has been very effective in studies of hydrocarbons but is not as good for molecules containing heteroatoms. This problem is a consequence of the neglect of one-center overlap in the INDO approximation on which MINDO/3 is based.$^{10}$

MINDO was developed on the NDDO approximation, and the main improvements over MINDO/3 were for aromatic compounds, molecules with triple bonds, three-membered rings, and molecules with N-N bonds.$^{11}$ These improvements have been attributed to the inclusion of directional effects in the two-center MINDO electron-electron repulsions and core-electron attractions. Dewar's group next developed AM1, a new parametrization based on the NDDO approximation, with a modified core repulsion function. This second generation modified NDDO method represented an improvement over MINDO, with the main benefit being more accurate estimates of activation energies for reactions.$^{12}$ Recently, a third generation modified NDDO molecular model, PM3, has been developed$^{12'}$ by using a new optimization procedure for quickly determining atomic parameters from experimental reference data. With this method the average difference between calculated heats of formation and experimental values for 657 compounds is 7.8 kcal/mol, as compared to 12.7 and 13.9 kcal/mol for AM1 and MINDO, respectively.$^{13}$ PM3 is particularly better than the prior methods for heat of formation calculations of hypervalent species.

In this study MOPAC 5.0 software$^{15}$ has been utilized to calculate the heats of formation ($\Delta H^o_{298}$) and geometries for CH$_2$OH, NO, and NO$_2$. Fully optimized geometries have also been obtained for the products and transition states formed in the reactions of the hydroxymethyl radical with NO and NO$_2$. No assumptions were made concerning the geometry of the transition state. The transition state both corresponds to a stationary point on the potential energy surface and is a saddle point (not the top of a hill). Saddle points are calculated within MOPAC by the procedure of McIver and Komornicki, by calculating and diagonalizing the Hessian matrix, or by Bartel's method, a nonlinear least-squares gradient minimization routine.$^{15}$ The force constant matrix at the transition state must have one and only one negative value in order to characterize the geometry as a saddle point. Restricted Hartree-Fock calculations were performed using both the AM1 and PM3 Hamiltonians. The criteria for terminating all optimizations was increased 100-fold over the normal MOPAC limits, and vibrational frequencies were calculated for each species to characterize ground and transition states. All calculations were carried out on a microVAX 3400 at Lake Forest College.

Results and Discussion

Results of MOPAC calculations using the AM1 and PM3 Hamiltonians are presented in Tables I and II. Table I lists calculated and experimental heats of formation for reactants and potential products which would be formed by reactions 1-3. It should be noted that in most cases the PM3 calculations are closer to the experimental heats of formation than the AM1 values. Indeed, for the seven molecules where experimental numbers are available, the average error in the heats of formation are 18.8 kcal mol$^{-1}$ for AM1 and 8.6 kcal mol$^{-1}$ for PM3.

The major differences between the AM1 and PM3 calculated values are for NO, NO$_2$, HNO, HOCH$_2$NO, HOCH$_2$ON, and HOCH$_2$CH$_2$OH, where the difference between the two methods ranges from 11 to 15 kcal mol$^{-1}$ and for HONO and HOCH$_2$ONO, where the method differs by approximately 24 and 38 kcal mol$^{-1}$, respectively. For every one of these species the PM3 calculation yields a higher energy value than the corresponding

**Table I: Calculated and Experimental Heats of Formation for Reactants ($\Delta H^o_{298}$) and Potential Products in Reactions of Gaseous CH$_2$OH with NO, NO$_2$, and CH$_3$OH**

<table>
<thead>
<tr>
<th>molecule</th>
<th>AM1 $\Delta H^o_{298}$ (kcal/mol)</th>
<th>PM3 $\Delta H^o_{298}$ (kcal/mol)</th>
<th>$\Delta H^o_{298}$ (kcal/mol)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$OH</td>
<td>-26.5</td>
<td>-23.5</td>
<td>-6.2</td>
<td>16</td>
</tr>
<tr>
<td>NO</td>
<td>1.2</td>
<td>14.7</td>
<td>21.6</td>
<td>11</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>-15.0</td>
<td>-1.0</td>
<td>7.91</td>
<td>17</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>-34.1-14.1</td>
<td>-26.0</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HNO</td>
<td>2.2</td>
<td>13.8</td>
<td>23.8</td>
<td>17</td>
</tr>
<tr>
<td>HON</td>
<td>42.4</td>
<td>49.0</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HOCH$_2$NO</td>
<td>-45.2</td>
<td>-33.8</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HOCH$_2$ON</td>
<td>-8.4</td>
<td>4.8</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>-13.6</td>
<td>-17.6</td>
<td>-14.9</td>
<td>17</td>
</tr>
<tr>
<td>HONO</td>
<td>-39.4-14.9</td>
<td>-18.8</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HOCH$_2$NO</td>
<td>-57.1</td>
<td>-55.8</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HOCH$_2$ONO</td>
<td>-91.6</td>
<td>-53.2</td>
<td>-26.0</td>
<td>18</td>
</tr>
<tr>
<td>HOCH$_2$CH$_2$OH</td>
<td>-111.4</td>
<td>-98.6</td>
<td>-93.05,-92.6</td>
<td>19,20</td>
</tr>
</tbody>
</table>

(15) Stewart, J. J. P. *QCPE* 455. Available from Indiana University, Department of Chemistry, Bloomington, IN.
TABLE II: Calculated Heats of Formation for the Transition-State Structures Formed from Reactions of CH₂OH with NO, NO₂, and CH₂OH and Calculated Activation Energy Barriers and Overall Enthalpy Change for Reactions of CH₂OH

<table>
<thead>
<tr>
<th>reaction</th>
<th>AM1</th>
<th>PM3</th>
<th>AM1</th>
<th>PM3</th>
<th>AM1</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH₂OH + CH₂OH → HOCH₂CH₂OH</td>
<td>-103</td>
<td>-101</td>
<td>-57.3</td>
<td>-50.6</td>
<td>-58.3</td>
<td>-51.0</td>
</tr>
<tr>
<td>2a. CH₂OH + NO → CH₂O + HNO</td>
<td>13.2</td>
<td>30.1</td>
<td>38.5</td>
<td>38.9</td>
<td>4.0</td>
<td>-11.5</td>
</tr>
<tr>
<td>2c. CH₂OH + NO → HOCH₂NO</td>
<td>-44.1</td>
<td>-31.4</td>
<td>-18.8</td>
<td>-22.6</td>
<td>-19.9</td>
<td>-25.0</td>
</tr>
<tr>
<td>2d. CH₂OH + NO → CH₂O + HONO</td>
<td>45.1</td>
<td>a</td>
<td>70.4</td>
<td>a</td>
<td>36.2</td>
<td>23.7</td>
</tr>
<tr>
<td>3a. CH₂OH + NO → CH₂O + HONO</td>
<td>-6.4</td>
<td>6.8</td>
<td>18.9</td>
<td>15.6</td>
<td>16.9</td>
<td>13.6</td>
</tr>
<tr>
<td>3b. CH₂OH + NO → HOCH₂NO₂</td>
<td>-35.5</td>
<td>-22.7</td>
<td>5.0</td>
<td>1.8</td>
<td>-16.6</td>
<td>-31.3</td>
</tr>
<tr>
<td>3c. CH₂OH + NO → HOC₂HON</td>
<td>-43.8</td>
<td>-18.3</td>
<td>-3.3</td>
<td>6.2</td>
<td>-51.1</td>
<td>-28.7</td>
</tr>
<tr>
<td>3d. CH₂OH + NO → CH₂O + HONO₂</td>
<td>-51.0</td>
<td>-53.5</td>
<td>-10.5</td>
<td>-29.0</td>
<td>-4.6</td>
<td>-27.2</td>
</tr>
</tbody>
</table>

*Unable to locate the saddle point for reaction 2c using PM3. †All values in kcal/mol.

AM1 number, bringing the semiempirical calculations closer to the experimental results. For HONO, the AM1 calculation gives a heat of formation of -39.4 kcal mol⁻¹ while the PM3 calculation results in a heat of formation of -14.9 kcal mol⁻¹. This result, where the PM3 number is quite close to the experimental value of -18.8 kcal mol⁻¹, illustrates how the improved parameterization of this reaction constructed to establish the PM3 Hamiltonian minimizes errors for systems where AM1 gives large deviations from experimental values. Table I shows similar behavior for NO, NO₂, and HNO, where the AM1 values deviate from experiment by 20–25 kcal mol⁻¹ and the corresponding PM3 values deviate by approximately 7–10 kcal mol⁻¹.

Historically, Dewar’s semiempirical methods¹⁰⁻¹² have reproduced heats of formation for diatomic and triatomic molecules rather poorly. This was not considered a major problem since the object of these methods has been to reproduce the chemistry of a wide range of organic compounds. The great success of the MINDO/3 and MNDO methods results from the fact that they reproduce molecular properties fairly accurately for a wide range of molecules, most of which were not included in the initial parameterization of the methods. While one could develop a semiempirical method that could accurately reproduce the heats of formation for, say, NO, NO₂, and HNO, the method would have limited utility to chemists in general if it could not successfully handle other classes of compounds. It should be noted that the latest MNDO method, PM3, has lowered the error in heats of formation for both large molecules and smaller diatomics and triatomics.

It is interesting to compare heats of formation calculated by MOPAC with those computed by using Benson’s rules."²² Benson tabulated the heat of formation contribution for different bonds, so that the heat of formation for an entire molecule could be estimated by summing the contributions of all of the bonds in the molecule. Values of ΔH₂₀ are generally estimated within a few kcal mol⁻¹ although large errors result for compounds containing very electronegative groups such as NO₂.° A result attributed to the high polarity of the NO₂ group.¹¹ No contribution for the N=O bond to the heat of formation is given by Benson, although the (NO)₂ bond is listed with a value of 9.0 kcal mol⁻¹. Thus, the heats of formation for NO, HNO, HONO, HOCH₂NO, and HOCH₂CH₂OH cannot be determined by using Benson’s rules. Heats of formation calculated by using Benson’s rules for CH₂OH, NO₂, CH₂O, HNO, HONO, HOCH₂NO, HOCH₂ONO, and HOCH₂CH₂OH are -46.66, 9, -19.66, 6.4, -18, -28.3, -49.66, and -90.59 kcal mol⁻¹, respectively. Comparison of these estimates with the data in Table I shows that NO₂, HONO, and HOCH₂CH₂OH are described accurately with Benson’s rules while CH₂OH and CH₂O are not.

Transition-state heats of formation for each reaction are listed in Table II. A comparison of the energies of the reactants, products, and transition states for each possible reaction is shown with the help of figures. Figures 1–4 depict the energetics of the reactions of CH₂OH with NO and NO₂ for both the AM1 and PM3 calculations. The sum of the calculated heats of formation for the reactants is plotted on the left-hand side of each figure, the sum of the heats for the products is presented on the right-hand side, and the transition-state energies for each reaction are plotted in the middle.

CH₂OH and CH₂OH. It is known that reaction of CH₂OH with itself is fast. The figures illustrate that, indeed, a negative activation energy precedes the transition state for the mutual reaction

\[ CH₂OH + CH₂OH → HOCH₂CH₂OH \] (1)

The general experience is that raising the temperature of a reaction leads to an increase in the specific rate constants describing the reaction. Occasionally, such as in reaction 1, the opposite behavior is encountered whereby when the temperature is increased the reaction slows down. This behavior can be understood by taking a closer look at the meaning of activation energy.²² It can be shown that the experimental activation energy is simply the difference between the average energy of reacting molecules and the average energy of molecules in the system,

\[ E_a = \langle E \rangle_{\text{reacting}} - \langle E \rangle_{\text{nonreacting}} \]

This implies that the reacting hydroxymethyl radicals have less internal thermal energy than the product HOCH₂CH₂OH molecules. The negative activation energy, calculated from the transition-state structure of reaction 1, means that the rate of combination is higher for those radicals with less than average thermal energy. As the temperature is raised, the population of radicals with less than average thermal energy is decreased and the effective rate of combination decreases with it.²²

Table II summarizes the activation energy barriers and net energy requirements depicted in the figures. As can be seen for the CH₂OH/CH₂OH system, the activation energy for reaction is -57.3 and -50.6 kcal/mol for the AM1 and PM3 calculations, respectively. The overall energy output from this exothermic reaction is predicted to be 58.3 and 51.0 kcal/mol by these two methods.

CH₂OH and NO. In order to measure the kinetics of reactions of CH₂OH with targets other than itself, Pagsberg et al. used two different methods of analysis in order to account for reaction 2. They propose that this rate constant consists of a combination of the rate constants for the abstraction reactions 2a and the addition reaction 2b.

\[ CH₂OH + NO → CH₂O + HNO \] (2a)

\[ M → HOCH₂NO \] (2b)

We have also considered the corresponding abstraction/addition reactions where the oxygen atom of nitric oxide is the attacking atom

\[ CH₂OH + NO → CH₂O + HON \] (2c)

\[ M → HOCH₂ON \] (2d)

Table I illustrates that HNO is more stable than HON and HOCH₂NO is more stable than HOCH₂OH. Figure 1 displays the AM1 results from Tables I and II while Figure 2 displays the

Figure 1. AM1 heats of formation for reactants, products, and transition states for the CH$_2$OH/NO system. The sum of the calculated heats of formation for the reactants are plotted on the left, the sum of the heats of the products are plotted on the right, and the transition-state energy is plotted in the middle.

Figure 2. PM3 heats of formation for reactants, products, and transition states for the CH$_2$OH/NO system. The sum of the calculated heats of formation for the reactants are plotted on the left, the sum of the heats of the products are plotted on the right, and the transition-state energy is plotted in the middle.

PM3 results. The figures show that the addition reaction 2b is exothermic by approximately 20–25 kcal/mol and has a negative activation energy of roughly 20 kcal/mol. Reaction 2a is slightly exothermic but requires an activation energy of 38 kcal/mol to occur. An activation barrier of 15–19 kcal/mol is required for reaction 2d to occur, while reaction 2c is least likely to occur at room temperature. Numerical results from Figures 1 and 2 are listed in Table II. These findings lend support to the suggestion that the adduct product HOCH$_2$NO accounts for the residual ultraviolet spectrum in the pulse radiolysis experiment.

CH$_2$OH and NO$_2$. It has been proposed that reactions of the hydroxymethyl radical with nitrogen dioxide which account for the measured rate constant of 2.3 × 10$^{-11}$ are

\[
\text{CH}_2\text{OH} + \text{NO}_2 \rightarrow \text{CH}_2\text{O} + \text{HONO} \quad (3a)
\]

\[
\text{M} \rightarrow \text{HOCH}_2\text{NO}_2 \quad (3b)
\]

\[
\text{M} \rightarrow \text{HOCH}_2\text{ONO} \quad (3c)
\]

In addition to these reactions, the reaction

\[
\text{CH}_2\text{OH} + \text{NO}_2 \rightarrow \text{CH}_2\text{O} + \text{HNO}_2 \quad (3d)
\]

is considered in this work. Table I shows that nitrous acid, a product in reaction 3a, is more stable than HNO$_2$ by the AM1 calculations but a little less stable by PM3. The experimental heat of formation for HONO agrees well with the PM3 value. The adduct product HOCH$_2$ONO is again more stable than HOCH$_2$NO$_2$ by AM1, but has about the same stability by the PM3 method. The energetics in Table I and II are displayed pictorially in Figures 3 and 4 for the AM1 and PM3 calculations, respectively. Figure 3 illustrates that reactions 3a, 3c, and 3d have negative activation energies. Reaction 3b has an activation energy of just 5 kcal/mol. All four reactions are exothermic. Figure 4 shows the results of the PM3 calculations. In this case, only reaction 3d has a negative activation energy, while reactions 3b and 3c require 2 and 6 kcal/mol for activation. It is of interest to note that reaction 3a to produce nitrous acid is least likely to occur according to the PM3 calculations. The energies depicted in Figures 3 and 4 are also summarized in Table II.

Much of the discrepancy between the AM1 and PM3 calculations is a consequence of the differences in calculated heats of formation for NO$_2$ and HONO. For instance, the reactants CH$_2$OH and NO$_2$ have a combined heat of formation of −41.5 kcal/mol when calculated by the AM1 method, but only −24.5 by PM3. This difference stems mainly from the calculated heat for NO$_2$, which is −15 kcal/mol for AM1 and −1 kcal/mol for
PM3. The experimental heat of formation for NO$_2$ of 7.9 kcal/mol is closest to the PM3 value. For reaction 3a, not only is the value of the sum of the heats of formation for the reactants off by 17 kcal/mol but also the sum of the heats of formation for the products is off by approximately 22 kcal/mol. This product difference stems from the difference in the heat of formation for nitrous acid. As listed in Table I, the experimental heat of formation for HONO is $-18.8$ kcal/mol, which compares favorably with the PM3 value of $-14.9$ kcal/mol.

The new parametrization routine used to produce the PM3 Hamiltonian has been shown to be more accurate than the previous semiempirical methods for many different types of molecules. Our findings for the CH$_3$OH system support this conclusion. Evaluating the results of the transition-state energies is more difficult as experimental information for activation barriers is not readily available. However, the information presented in Figures 3 and 4 allow us to describe an experiment that may help determine which method has correctly predicted the activation barriers. If the kinetics experiments were repeated at lower temperatures, insight could be gained on the behavior of the CH$_3$OH system. If the CH$_3$OH/NO$_2$ system is described most accurately by the PM3 calculations outlined in Figure 4, then lowering the temperature should decrease the rate constant as reactions 3a, 3b, and 3c would contribute less and less at lower temperatures. On the other hand, Figure 3 shows that three of the four reactions have negative activation energies. Lowering the temperature in this case should not decrease the rate constant in the same manner as in the PM3 case.

This same experimental technique of measuring rate constants at lower temperatures can also be used for the NO system. In this case, such experimental measurements would show whether reaction 2b is indeed the dominant reaction in the system. If it is, then the rate constant will not decrease with lower temperatures and reactions 2a, 2c, and 2d will be shown to have a small contribution to the overall rate constant.

**Conclusion**

The AM1 and PM3 molecular orbital methods have been utilized to investigate the reactions of CH$_3$OH with NO and NO$_2$. For ground-state structures the PM3 method is superior for these systems. Both AM1 and PM3 predict that the dominant reaction of CH$_3$OH with NO produces the adduct HOCH$_2$NO supporting the hypothesis from the pulse radiolysis/kinetic analysis experiments. For the NO$_2$ system the calculations predict the formation of HOCH$_2$NO$_2$ and HOCH$_2$ONO. Furthermore, the PM3 calculations predict that formation of CH$_2$O and HNO$_2$ is much more likely than the formation of CH$_2$O and HONO from reactions of the hydroxymethyl radical with nitrogen dioxide.

**Acknowledgment.** We thank Jim Oddo for technical assistance. This work was supported by a Bristol-Myers Co. Grant of Research Corporation.

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**Ab Initio Molecular Orbital Study of Adducts and Oxides of Boron Hydrides**

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(Received: October 12, 1990)

Ab initio molecular orbital theory at the HF/6-31G* level has been used to investigate the structures of Lewis acid/base adducts of boron hydrides with argon and a variety of substrates that may be encountered in the mechanism for the oxidation of diborane. By use of fourth-order Moller–Plesset theory, i.e., MP4SDTQ, correlation effects are calculated at the HF/6-31G* geometries. Borane was found to form stable adducts with dioxygen, hydroxyl radical, OCP) atom, and H–B==O. Structures of isomeric forms of HBO, H$_2$BO, H$_3$BO, H$_4$BO$_2$, H$_5$BO$_3$, H$_5$BO$_4$, H$_5$BO$_6$, H$_5$BO$_8$, and cyclic (HBO)$_3$ were investigated. Evidence is presented for Lewis acid/base adducts with BH$_3$ radical and some oxygenated boranes. The number and stability of these adducts suggest that the mechanism of the oxidation of diborane is much more complicated than that of ethane where adduct formation can be neglected.

**Introduction**

Borane chemistry is very rich and much studied. Since boron has only five electrons, early theoretical studies focused on simple boron hydrides, BH, BH$_2$, and BH$_3$, because these could be studied with the available computational facilities. The development of more sophisticated computers permitted treatment of molecules with more electrons, e.g., the adducts of BH$_4$, CO and NH$_3$, and diborane itself was examined. Diborane, H$_2$B($\mu$H)$_2$BH$_2$, is the prototype structure for $\mu$-hydrido bridging in electron-deficient systems. Consequently, the structural and electronic properties of this novel dimer have been studied extensively, both experimentally and computationally. A recent review has been published. Ab initio techniques are being used to unravel the complex kinetics of diborane pyrolysis, although the rate-determining step is still in doubt. Recent studies have found that the BH$_2$H$_2$

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(4) Ab Initio techniques are being used to unravel the complex kinetics of diborane pyrolysis, although the rate-determining step is still in doubt.
(5) Recent studies have found that the BH$_2$H$_2$ adduct is remarkably stable and that correlation effects are very important in determining the structure of triborane.
(6) Modeling of the oxidation has been recommended and used by Borchardt et al. to reproduce the OH radical profile generated by the reaction of O(\text{P}) atoms with diborane. This modeling was performed before it was recognized that the B$_2$H$_5$ radical could exist in isomeric forms and the

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