the reaction of OH with H₂. The value of $T^*$ for the latter reaction was also below the experimental temperature range. For the reaction of H with CH₃ we found a much higher barrier, 55 kJ mol⁻¹, but for Cl with CH₄, a somewhat lower barrier, 12 kJ mol⁻¹, with little tunneling.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada for financial support and H. Furue and A. Mehta for assistance with computations.

Registry No. OH, 3352-57-6; CH₄, 74-82-8.

Kinetics of the Reaction between OH and HO₂ on the Triplet Potential Energy Surface

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Ab initio and rate theory calculations are used to study the OH + HO₂ → O₂ + H₂O reaction. The structure and energy are determined for the planar HO–HO₂ hydrogen-bonded complex. At the highest level of theory considered here, PMP4/6-31G**, this complex is more stable than the separated reactants by 5.1 and 9.0 kcal/mol on the \( ^1\Sigma^+ \) and \( ^2\Pi \) potential energy surfaces, respectively. The \( ^2\Pi \) surface correlates with the ground electronic state products, and the energy and vibrational frequencies for the reaction transition state on this surface are calculated at the HF/6-31G** and MP2/6-31G** levels. In nonplanar configurations an avoided crossing occurs between the \( ^2\Pi \) and \( ^1\Sigma^+ \) surfaces. The nonplanar \( ^2\Pi \) transition state which arises from the planar \( ^2\Pi \) transition state is characterized at both the HF and MP2 levels. However, there is considerable uncertainty regarding the position of the \( ^2\Pi \rightarrow ^1\Sigma^+ \) avoided crossing. As a result, it is not clear whether the triplet reaction transition state originates from the planar \( ^2\Pi \) transition state or the \( ^2\Pi \rightarrow ^1\Sigma^+ \) avoided crossing. The reaction kinetics on the triplet surface is controlled by the long-range attractive potential and not by the reaction transition state. A vibrationally/rotationally adiabatic model, with proper treatment of electronic degeneracies, gives a reaction rate constant as a function of temperature which agrees within a factor of 2 with the most recent experimental results for the 298–1100 K temperature range. Combining this calculated temperature dependence with the average of all recent experimental measurements of the OH + HO₂ reaction rate at ambient temperature yields the rate constant \( k_1 = 7.1 \times 10^{-11} \exp[(250/298)/RT] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \) for the 254–382 K temperature range. These two expressions for \( k_1 \) differ by a factor of 1.6 at 300 K with their difference increasing as \( T \) increases. Also, neither of these expressions extend into the high-temperature regime of combustion studies.

Theoretical studies have been carried out to assist in interpreting the kinetics for reaction 1. The most extensive theoretical work has involved ab initio quantum chemical calculations. The OH + HO₂ singlet potential energy surface, the reactants associate to form the hydrogen trioxide intermediate H₂O₃. The potential energies and structures of different internal rotation

I. Introduction

The reaction

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  

(1)

is of interest because of its importance in atmospheric and combustion chemistry and because of its close relationship to peroxo–peroxy radical reactions. Reliable measurements of the rate constant for this reaction have proven difficult, particularly at elevated temperatures. The standard procedure for determining \( k_1 \) is to measure the loss of OH in excess HO₂. From early studies of this type there was some indication that \( k_1 \) is pressure dependent between 1 and 1000 Torr; increasing from (5-8) \( \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹ at low pressure to (1-2) \( \times 10^{-10} \) cm³ molecule⁻¹ s⁻¹ at high pressure. In recent work, Keyser measured \( k_1 \) as (1.1 ± 0.3) \( \times 10^{-10} \) cm³ molecule⁻¹ s⁻¹ at 299 K and 1 Torr and Schwab et al. found \( k_1 \) to equal (8.0 ± 2.0) \( \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹ at 298 K and 2 Torr. These low-pressure values for \( k_1 \) are not significantly different from the values measured at high pressure. Thus, the current experimental understanding of \( k_1 \) is that the rate constant for reaction 1 exhibits little or no pressure dependence for pressures less than 1000 Torr.

A more problematic issue regarding \( k_1 \) is its temperature dependence. This is particularly significant since reaction 1 is an important termination reaction in combustion mechanisms with fuel-lean conditions. The earliest determination of the temperature dependence of \( k_1 \) was by Sridharan et al., who found \( k_1 \) to equal (1.7 ± 0.5) \( \times 10^{-11} \) exp[(616 ± 86)/RT] cm³ molecule⁻¹ s⁻¹ for \( T = 252-420 \) K. In a more recent study Keyser found \( k_1 \) to equal (4.8 ± 0.8) \( \times 10^{-11} \) exp[(250 ± 50)/RT] cm³ molecule⁻¹ s⁻¹ for the 254–382 K temperature range. These two expressions for \( k_1 \) differ by a factor of 1.6 at 300 K with their difference increasing as \( T \) increases. Also, neither of these expressions extend into the high-temperature regime of combustion studies.

Theoretical studies have been carried out to interpret the kinetics for reaction 1. The most extensive theoretical work has involved ab initio quantum chemical calculations. On the OH + HO₂ singlet potential energy surface, the reactants associate to form the hydrogen trioxide intermediate H₂O₃. The potential energies and structures of different internal rotation

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conformations of H$_2$O$_3$ were studied by Cremer$^{13}$ using Hartree-Fock theory with basis sets with and without polarization functions. Electron correlation was treated via many-body perturbation theory. An important finding from this study is the large barriers for simultaneous rotation of both OH groups in hydrogen trioxide.

In a SCF-CI study utilizing basis sets of polarized double-$	frac{1}{2}$ quality, Jackels and Phillips$^{14}$ investigated both the HOOOO hydrogen trioxide intermediate and the HO-HO$_2$ hydrogen-bonded species. The trioxide intermediate was found to be nonplanar, in a $^1A_e$ electronic state, and to have an electronic energy 26.4 kcal/mol lower than that of the OH and HO$_2$ reactants. The hydrogen-bonded species was assumed to be planar and was found to have essentially degenerate $^1A_e$ and $^1A''_e$ states with an electronic energy 4.7 kcal/mol below that of the reactants. Geometries for the hydrogen-bonded $^1A_v$ and $^1A''_v$ excited states were not optimized, but a qualitative analysis showed that they are also bound.

In recent work Toohey and Anderson$^{15}$ studied the $^1A_v$ and $^1A''_v$ potential energy surfaces using HF and MP2 theory with the 3-21G** and 6-31G** basis sets. Using HF/6-31G** calculations, geometries were optimized for both the $^1A_v$ and $^1A''_v$ planar HO-HO$_2$ hydrogen-bonded species. The $^1A_v$ HO-HO$_2$ complex was found to have an electronic binding energy of 6.0 kcal/mol and to be 1.9 kcal/mol lower in energy than the $^1A''_v$ complex. The $^1A_v$ state correlates with the O$_2$ and HO$_2$ ground-state products, while the $^1A''_v$ state is correlated with excited triplet channels which are not energetically accessible at thermal energies. Toohey and Anderson$^{16}$ found a planar saddlepoint for reaction on the $^1A_v$ surface at the HF/3-21G**, HF/6-31G**, and MP2/6-31G** levels of theory. At the MP2/6-31G** level the transition state has an electronic energy 2.6 kcal/mol higher than that of the reactants. However, because of the size and temperature dependence of $k_v$, they concluded that the MP2 estimate of the saddlepoint energy is too high and crossing this saddlepoint energy is not rate determining.

Several theoretical studies have dealt with the kinetics of reaction 1. In a model RRKM study, which did not explicitly treat the different singlet and triplet potential energy surfaces involved in OH + HO$_2$ collisions, Mozerukewich$^{16}$ considered the pressure and temperature dependence of reaction 1. In this study it was assumed that the negative temperature dependence required either one or both of the following complex mechanisms:

$$\begin{align*}
\text{OH} + \text{HO}_2 &\rightarrow \text{HO}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad (2) \\
\text{OH} + \text{OH}_2 &\rightarrow \text{HOOOH} \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad (3)
\end{align*}$$

The hydrogen-bonded species was found to be too weakly bound to produce a significant pressure dependence. Reaction 3 had to be included in the overall mechanism to obtain an observable pressure dependence. In a calculation utilizing their ab initio perturbation theory, Kazachenko and Melius$^{17}$ found that the singlet potential surface and vibrational frequencies for reaction 2 gives an $A$ factor for reaction between OH and HO$_2$ substantially smaller than the experimental value. Phillips$^{17}$ has determined a rate constant for reaction 1 using a modified Langevin collision capture model based on the OH + HO$_2$ long-range potential and assuming reaction occurs on the singlet surface. Thus his calculated rate constant agrees with experiment at 300 K, its temperature dependence does not agree with experiment. Kelsey's recent experimental determination$^{1}$ of the temperature dependence of reaction 1 is $k_1 = (4.8 \pm 0.8) \times 10^{-11} \exp(250 \pm 50)/T$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $T = 254^{-382}$ K. In contrast, Phillips' theoretical model gives $k_1 = 7.5 \times 10^{-11} \exp(76/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $T = 250^{-400}$ K.

In very recent work we performed electronic structure and reaction rate theory calculations to study reaction 1 on the singlet potential energy surface. Structures for the HOOOO hydrogen trioxide intermediate and the reaction transition state for $^1O_2 + H_2O$ formation were optimized using HF/6-31G** and MP2/6-31G** theory. MP4 theory with the 6-31G** basis was then used to calculate energies for the MP2 optimized structures. The MP4 0 K barrier height for the reaction transition state is 15.2 kcal/mol. Thus, reaction on the singlet surface to form $^1O_2$ and $H_2O$ is predicted to be unimportant, except at highly elevated temperature. Vibrational quenching of the HOOOH intermediate formed by OH + HO$_2$ association would lead to the loss of OH and an apparent pressure enhancement of the reaction rate. However, because of the rather shallow potential energy minimum found for HOOH (i.e., $\sim 20^{-30}$ kcal/mol),$^{14}$ helium pressures in excess of 5000 Torr are required to yield noticeable stabilization of HOOH at room temperature (higher temperatures would require higher pressures for stabilization). From our calculations it was concluded that for pressures in the range of several atmospheres and less and for temperatures below 2500 K, OH + HO$_2$ collisions on the singlet surface do not lead to appreciable reaction or loss of reactants. Thus, any reaction for these pressure and temperature conditions is predicted to occur on the triplet potential energy surface. In this paper we present electronic structure and reaction rate theory calculations for reaction 1 on the triplet potential energy surface.

II. Ab Initio Calculations of the Triplet Potential Energy Surfaces

A. Theoretical Method. Ab initio molecular orbital calculations were performed using the GAUSSIAN 88 and 90 system of programs. Fully optimized geometries, harmonic vibrational frequencies, and zero-point energy corrections for the reactants, intermediates, transition structures, and products involved in the reaction between HO$_2$ and OH (on the triplet surface) were calculated at the Hartree-Fock and MP2 levels using the 6-31G** basis set$^{20}$ with analytical derivatives.$^{21}$

Electron correlation was computed with fourth-order Möller-Plesset perturbation theory$^{22}$ in the space of single, double, triple, and quadrupole excitations using the optimized geometries obtained at the Hartree-Fock and MP2 levels (MP4SDTQ/6-31G**//HF/6-31G** and MP4SDTQ/6-31G**//MP2/6-31G**, respectively). Since the energies were calculated by unrestricted HF and MPn methods, an approximate spin projection method$^{23}$ was used to remove contamination from higher spin states (denoted by PMPn in Table I).

B. Planar $^1A_v$ Potential Energy Surface. Both HF and MP2 optimized structures for stationary points on the planar $^1A_v$ potential energy surface were obtained using the GAUSSIAN 88 and 90 system of programs. Fully optimized geometries, harmonic vibrational frequencies, and zero-point energy corrections for the reactants, intermediates, transition structures, and products involved in the reaction between HO$_2$ and OH (on the triplet surface) were calculated at the Hartree-Fock and MP2 levels using the 6-31G** basis set$^{20}$ with analytical derivatives.$^{21}$

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Reaction between OH and HO$_2$

The Journal of Physical Chemistry, Vol. 96, No. 4, 1992 1769

Figure 2. Calculated HF and MP2 (indicated by asterisks) geometries for the planar 3A'' reaction transition state.

Table I: Structures and Energies for the Planar 3A'' Potential Energy Surface

<table>
<thead>
<tr>
<th>coordinate*</th>
<th>reactants</th>
<th>complex</th>
<th>trans state</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>0.971 (0.955)$^a$</td>
<td>0.970 (0.954)</td>
<td>0.973 (0.953)</td>
<td>0.960 (0.943)</td>
</tr>
<tr>
<td>$R_2$</td>
<td>2.016 (2.078)</td>
<td>1.332 (1.240)</td>
<td>1.332 (1.240)</td>
<td>0.960 (0.943)</td>
</tr>
<tr>
<td>$R_3$</td>
<td>0.975 (0.950)</td>
<td>0.977 (0.951)</td>
<td>1.064 (1.114)</td>
<td>1.064 (1.114)</td>
</tr>
<tr>
<td>$R_4$</td>
<td>1.325 (1.309)</td>
<td>1.322 (1.308)</td>
<td>1.289 (1.259)</td>
<td>1.246 (1.168)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>138.2 (174.0)</td>
<td>99.1 (101.7)</td>
<td>103.8 (106.0)</td>
<td>103.8 (106.0)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>133.7 (171.8)</td>
<td>160.2 (167.6)</td>
<td>107.9 (109.9)</td>
<td>107.9 (109.9)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>104.5 (105.9)</td>
<td>103.6 (105.7)</td>
<td>107.9 (109.9)</td>
<td>107.9 (109.9)</td>
</tr>
</tbody>
</table>

*Bond distances are in units of angstroms and angles in degrees. Using the atom numbering H$_2$O$_2$H$_3$O$_4$, the internal coordinates are defined as follows: $R_1 = H_2O_2, R_2 = O_2H_3, R_3 = H_2O_4, R_4 = O_2H_3, \alpha = H_1O_2H_3, \beta = O_2H_3O_4$, and $\gamma = H_1O_2O_4$. $^a$ Both MP2/6-31G** and HF/6-31G** optimized geometries are given. The HF geometries are in parentheses. *Energies are given in hartrees (1 hartree = 62.75 kcal/mol). The HF energies are calculated at the HF geometries. The remaining energies are calculated at the MP2 geometries. The MP2 energy is full; the energies are calculated at the MP2 geometries. The MP2 energy is full. $^{b}$ The OH and HO$_2$ individual energies are given in ref. 18. $^c$ The OH and HO$_2$ individual energies are given in ref. 18. $^d$ The O$_2$ energies are given in parentheses. The HO$_2$ energies are given in ref. 18. $^e$ The OH and HO$_2$ individual energies are given in ref. 18. $^f$ The O$_2$ energies are given in parentheses. The HO$_2$ energies are given in ref. 18.

Table II: MP2 and HF Vibrational Frequencies for the Planar 3A'' Potential Energy Surface

<table>
<thead>
<tr>
<th>motion</th>
<th>reactants</th>
<th>complex</th>
<th>trans state</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch</td>
<td>3847 (4052)</td>
<td>(4068)</td>
<td>(4086)</td>
<td>4033 (4264)$^a$</td>
</tr>
<tr>
<td>O-O stretch</td>
<td>(157)</td>
<td>(636)</td>
<td>3895 (4147)</td>
<td></td>
</tr>
<tr>
<td>O-H stretch</td>
<td>3713 (4074)</td>
<td>(4073)</td>
<td>(5185)</td>
<td></td>
</tr>
<tr>
<td>O-H bend</td>
<td>1248 (1251)</td>
<td>(1259)</td>
<td>(1380)</td>
<td></td>
</tr>
<tr>
<td>O-O-H bend</td>
<td>1460 (1602)</td>
<td>(1645)</td>
<td>(1636)</td>
<td></td>
</tr>
<tr>
<td>O--O-H bend</td>
<td>(265)</td>
<td>(867)</td>
<td>1684 (1770)</td>
<td></td>
</tr>
<tr>
<td>O--O-H bend</td>
<td>(356)</td>
<td>(999)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Frequencies are in cm$^{-1}$. The MP2/6-31G** and HF/6-31G** (in parentheses) vibrational frequencies were calculated at the MP2 and HF optimized geometries, respectively. $^b$ The A' and A'' symmetries refer to the complex and transition-state vibrations.
TABLE III: Relative Electronic Energies for the Planar \( ^{1}A' \) Potential Energy Surface

<table>
<thead>
<tr>
<th>theory</th>
<th>reactants</th>
<th>complex</th>
<th>trans state</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0</td>
<td>-4.11</td>
<td>19.97</td>
<td>-48.04</td>
</tr>
<tr>
<td>MP2</td>
<td>0</td>
<td>-5.47</td>
<td>2.49</td>
<td>-81.05</td>
</tr>
<tr>
<td>MP3</td>
<td>0</td>
<td>-4.98</td>
<td>5.75</td>
<td>-66.87</td>
</tr>
<tr>
<td>MP4</td>
<td>0</td>
<td>-5.35</td>
<td>2.24</td>
<td>-72.06</td>
</tr>
<tr>
<td>PHF</td>
<td>0</td>
<td>-2.45</td>
<td>14.54</td>
<td>-44.20</td>
</tr>
<tr>
<td>PMP2</td>
<td>0</td>
<td>-4.85</td>
<td>1.84</td>
<td>-83.97</td>
</tr>
<tr>
<td>PMP3</td>
<td>0</td>
<td>-4.69</td>
<td>5.18</td>
<td>-67.04</td>
</tr>
<tr>
<td>PMP4</td>
<td>0</td>
<td>-5.05</td>
<td>1.67</td>
<td>-72.23</td>
</tr>
</tbody>
</table>

*Zero-point energies are not included. Energies are in kcal/mol.

Figure 3. Comparison between HF and MP2 geometries for the \( ^{1}A' \) and \( ^{3}A' \) hydrogen-bonded complexes.

TABLE IV: Geometry and Energy of the Planar \( ^{3}A' \) Complex

<table>
<thead>
<tr>
<th>coordinate*</th>
<th>HF(^{b})</th>
<th>MP2(^{b})</th>
<th>ref 14 (HF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 )</td>
<td>0.957</td>
<td>0.978</td>
<td>0.957</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>2.075</td>
<td>1.943</td>
<td>2.003</td>
</tr>
<tr>
<td>( R_3 )</td>
<td>0.954</td>
<td>0.984</td>
<td>0.953</td>
</tr>
<tr>
<td>( R_4 )</td>
<td>1.306</td>
<td>1.317</td>
<td>1.305</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>91.9</td>
<td>80.5</td>
<td>104.3</td>
</tr>
<tr>
<td>( \beta )</td>
<td>144.0</td>
<td>140.6</td>
<td>147.5</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>105.1</td>
<td>103.5</td>
<td>104.5</td>
</tr>
</tbody>
</table>

\(^{a}\)Bond lengths and angles are in units of angstroms and degrees, respectively. The coordinates are defined in footnote \( a \) of Table I. \(^{b}\)The 6-31G** basis set was used for the HF and MP2 calculations.

\( ^{3}A' \) complexes is greater in the MPn than HF calculations may result from the different effects treating electron correlation has on the geometries of these two complexes. For the \( ^{3}A' \) complex the MP2 O-H distance is 0.06 Å shorter than is the HF O-H distance. The difference between the MP2 and HF O-H distances is larger, i.e., 0.13 Å, for the \( ^{3}A' \) complex. Thus, if shortening of the O-H distance by MP2 theory leads to an increased stability of the computationally MP2 geometry, optimization will stabilize the \( ^{3}A' \) complex more than the \( ^{3}A' \) complex.

In previous work Toohey and Anderson\(^{15}\) also calculated the geometry and energy of the \( ^{1}A' \) complex using HF/6-31G** theory. Our results in Table IV for this level of theory are identical to what they reported. Jackels and Phillips\(^{14}\) performed the first ab initio study of the \( ^{1}A' \) complex. The geometry they found is listed in Table IV. It was determined using HF theory and the standard 6-31G** basis set, except that the polarization functions were chosen to have exponents of 0.85 on oxygen and 1.0 on hydrogen instead of the standard values of 0.8 and 1.1, respectively. These different polarization function exponents explain why their HF optimized \( ^{1}A' \) hydrogen-bonded complex has a slightly different geometry than does ours. Including triples in the MP4 calculation lowers the barrier. For the \( ^{3}A' \) transition state for the lowest energy \( ^{3}A' \) surface arises from the

Reaction between OH and HO₂

planar transition state for the 3A'' surface. However, if the avoided crossing occurs after the planar 3A'' transition state is reached, the remnants of the planar 3A'' transition state are now calculated at this level of theory, the 'A' surface is 2.1 kcal/mol occurs before the 3A'' transition state is reached. At the HF/planar transition state for the 3A'' surface. However, if the avoided crossing in Figure 4. Therefore, the nonplanar 'A potential energy surfaces are like those originating from the planar 3A'' transition state.

Figure 4. Two possible 3A'-3A'' surface crossings.

Figure 5. Nonplanar avoided crossings for the 3A'-3A'' surface crossings in Figure 4.

Table V: Comparison of the Planar 3A'' Transition State and the Nonplanar 3A Transition State Originating from the Planar 3A'' Transition State

<table>
<thead>
<tr>
<th>coordinate</th>
<th>planar</th>
<th>nonplanar</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ₁</td>
<td>0.0 (0.0)</td>
<td>4.8 (4.8)</td>
</tr>
<tr>
<td>θ₂</td>
<td>0.0 (0.0)</td>
<td>81.0 (81.0)</td>
</tr>
<tr>
<td>R₁</td>
<td>0.973 (0.953)</td>
<td>0.972 (0.953)</td>
</tr>
<tr>
<td>R₂</td>
<td>1.329 (1.240)</td>
<td>1.339 (1.238)</td>
</tr>
<tr>
<td>R₃</td>
<td>1.059 (1.113)</td>
<td>1.059 (1.113)</td>
</tr>
<tr>
<td>R₄</td>
<td>1.297 (1.260)</td>
<td>1.297 (1.260)</td>
</tr>
<tr>
<td>α</td>
<td>99.1 (101.7)</td>
<td>105.8 (103.5)</td>
</tr>
<tr>
<td>β</td>
<td>160.2 (167.6)</td>
<td>160.0 (165.8)</td>
</tr>
<tr>
<td>γ</td>
<td>107.7 (109.9)</td>
<td>106.9 (108.6)</td>
</tr>
</tbody>
</table>

Frequencies:
- HF: 2130i (5185) 221i (2329)
- MP2: 3824 (4086) 3860 (4087)
- MP3: 2449 (1636) 3635 (1379)
- MP4: 2297 (1380) 1452 (1363)
- PHF: 1761 (867) 1274 (1310)
- PMP2: 1464 (647) 710 (737)
- PMP3: 705 (636) 396 (466)
- PMP4: 423 (189) 297 (221)
- PMP4: 256i (991) 102 (100)

Energies:
- HF: -225.533 14 -225.533 44
- MP2: -226.043 64 -226.043 00
- MP3: -226.051 77 -226.051 54
- MP4: -226.077 61 -226.077 00
- PHF: -225.547 23 -225.548 12
- PMP2: -226.041 38 -226.040 38
- PMP3: -226.054 77 -226.054 34
- PMP4: -226.080 61 -226.079 80

*a = H₄O⁻H₂O₂ dihedral and θ₂ = O₂⁻H₃O⁺O₂ dihedral. The remaining coordinates are defined in footnote a of Table I. Bond distances are in units of angstroms and angles in degrees. bBoth MP2/6-31G** and HF/6-31G** optimized geometries are given. The HF geometries are in parentheses. cSee footnote c of Table I. dSevere SCF convergence difficulties (probably due to the proximity of the two states as shown in Figure 5) as well as the flatness of the potential energy surface with respect to the dihedral angles θ₁ and θ₂ prevented the usual convergence on the optimized geometry. With θ₁ and θ₂ fixed at their HF optimized values, the maximum gradient (0.000 40 au) and RMS gradient (0.000 15 au) of the MP2 optimized structure were below the usual thresholds. From further attempts at optimization, we estimate the uncertainty in θ₁, θ₂, and the MP2 energy to be ±10°, ±40°, and ±0.001 au, respectively.

Figure 6. Calculated HF and MP2 (indicated by asterisks) geometries for the nonplanar 3A transition state, which originates from the planar 3A'' transition state.
planar \(^1A^\prime\) and nonplanar \(^1A\) transition states. The difference between the HF and MP2 geometries for the nonplanar transition state is the same as discussed above for the planar transition state. The MP2 calculation gives a much earlier transition state than does the HF calculation. A major difference between the planar and nonplanar transition states, at both the HF and MP2 levels of theory, lies in their vibrational frequencies. The planar \(^1A^\prime\) and nonplanar \(^1A\) transition states have very similar energies, with the nonplanar one lower by 0.19 kcal/mol at both the HF and MP2 levels as \(\theta_i\) is changed from 0 to 90°.

This nonplanar \(^1A\) transition state will be the OH + HO\(_2\) \(\rightarrow\) H\(_2\)O + O\(_2\) reaction transition state if the \(^3A^\prime\) and \(^1A\) surfaces cross as shown in Figure 4a to give the nonplanar \(^1A\) surfaces shown in Figure 5a. As discussed in section II.D, calculations with HF/6-31G** geometries and energies and MP2/6-31G** geometries and energies show that the \(^1A^\prime\) to \(^1A\) crossing is that given in Figure 4a. However, we do not feel the calculations reported here are sufficiently quantitative to rule out the possibility that the actual \(^1A^\prime\) to \(^1A\) crossing occurs after the \(^1A^\prime\) transition state. Second-order Møller–Plesset perturbation theory probably does not adequately treat the coupling between the \(^3A^\prime\) and \(^1A\) surfaces in nonplanar configurations, and a multi-reference CI calculation may be necessary for a proper representation of this coupling. If the crossing occurs after the \(^1A^\prime\) transition state, the nonplanar \(^1A\) transition state found here will not be the reaction transition state.

### III. Reaction Kinetics

#### A. Ab Initio Rates

The ab initio calculations reported here give a transition state for reaction on the triplet surface with a potential energy greater than that of the reactants. Thus, these calculations predict a positive activation energy for reaction in contrast to the negative activation energy observed in experimental measurements\(^1\) of the reaction rate.

The nonplanar MP2 transition-state structure, MP2 vibrational frequencies, and MP4 transition-state energy (Table V), when combined with the MP2 reactant properties (Tables I and II), give a transition-state theory rate constant for reaction 1 at 300 K of \(1.2 \times 10^{-13}\) cm\(^3\)/molecule \(s^{-1}\), with Arrhenius parameters of \(A = 4.7 \times 10^{-13}\) cm\(^3\)/molecule \(s^{-1}\) and \(E_a = 3.58\) kcal/mol. These rate parameters differ sharply with those found in the most recent experimental determination\(^1\) of \(k_i\) for the 254–382 K temperature range; i.e., \(k_i = (4.8 \pm 0.8) \times 10^{-11}\) exp\((250 \pm 50)/RT\) cm\(^3\)/molecule \(s^{-1}\). The ab initio rate constant is too small by 4 orders of magnitude, which results from an ab initio \(A\) factor and activation energy that are too small and too large, respectively. Thus, the ab initio transition state is tighter and has a higher potential energy than the one that controls the experimental reaction rate.

The above analysis indicates that the kinetics for the experimental reaction is not controlled by a transition state along the reaction path which has properties like those of the ab initio transition state found here. One way to ensure that crossing this transition state is not rate controlling is to simply lower its potential energy. If the MP2 transition-state structure and vibrational frequencies are assumed as above, the transition state's electronic potential energy relative to reactants must be lowered by 7.5 kcal/mol to –3.8 kcal/mol to obtain a rate constant which agrees with the experimental value of 9.2 \(\times 10^{-11}\) cm\(^3\)/molecule \(s^{-1}\) determined by Keyser\(^1\) at the highest temperature he investigated of 382 K. At lower temperatures this modified transition state gives rate constants larger than the experimental values so that crossing this modified ab initio transition state is not rate controlling for all temperatures in the range investigated by Keyser.

#### B. Vibrational/Rotation Adiabatic Capture Rate Constant

If the tight ab initio transition state discussed above does not control the rate of reaction 1, the rate must be controlled by the long-range interaction between OH and HO\(_2\). A model for this interaction is the dipole–dipole intermolecular potential,\(^5\) which is given by

\[
\langle\mu \cdot \mu^* / R^3\rangle [2 \cos \theta_i \cos \theta_2 - \sin \theta_i \sin \theta_2 \cos (\phi_i - \phi_2)]
\]

In this equation \(\mu\) is the absolute magnitude of the dipole moment and \((\theta_i, \phi_i)\) refer to the spherical polar angles describing the orientation of \(r_i\) with respect to the body-fixed axes, for molecule \(i\). This equation provides a basis for calculating a capture rate constant\(^2\) for OH + HO\(_2\) association. Capture supposedly occurs when the reactive system moves inside a critical value for the center of mass separation \(R\) between the two molecules. After capture, it is assumed the reactive system forms the \(^3\)O\(_2\) + H\(_2\)O products with unit efficiency.

There are different theoretical approaches for calculating the capture rate constant. One could use either microcanonical or canonical variational transition-state theory (VTST), with the canonical version giving an upper bound to the more accurate microcanonical rate constant. A Langevin type classical mechanical theory\(^2\) can also be used to calculate the capture rate constant. Here we use vibrationally/rotationally adiabatic theory to calculate the capture rate constant. In this theory it is assumed that quantum numbers for reactant energy levels can be used to label adiabatic potential energy curves versus reactant separation and that the reactive system stays on the same energy curve with fixed quantum numbers until the critical reactant capture radius is attained. A properly evaluated vibrationally/rotationally adiabatic rate constant will be less than or equal to that of microcanonical VTST.

For the dipole–dipole potential in eq 4 the vibrationally/rotationally adiabatic capture rate constant is found to be\(^2\)

\[
k(T) = p(T) / T^{1/2} \frac{Q_{OH}Q_{HO}}{Q_{HO2}}
\]

where \(p(T)\) is the probability the collision occurs on the reaction potential energy surface,\(^3\) \(\mu\) is the reactant reduced mass, and \(k_B\) is the Boltzmann constant. The term \(p(T)\) is the electronic partition function ratio and, for OH + HO\(_2\), is given by

\[
p(T) = \frac{g_1}{Q_{OH}Q_{HO}}
\]

For OH + HO\(_2\) association, reaction occurs on a \(^3\)A potential energy surface so that \(g_1 = 3\). The ground state of HO\(_2\) has \(^2\)A\(\prime\) symmetry and the \(^2\)A\(\prime\) first excited state is approximately 17 kcal/mol higher in energy,\(^5\) so that for thermal energies \(Q_{HO2}\) is 2. The OH radical has \(^2\)Π\(\prime\) and \(^2\)Π\(\prime\) low-lying spin–orbit states, with the \(^2\)Π\(\prime\) state 205 R higher in energy.\(^5\) Thus

\[
Q_{OH} = 2 + 2 \exp(-205/T)
\]

\[
p(T) = \frac{3}{2[2 + 2 \exp(-205/T)]}
\]

Theoretical values for \(k\) are determined by inserting eq 8 into eq 7 and using the HO\(_2\) and OH dipole moments of 2.09 and 1.67 D, respectively. The resulting rate constants versus temperature are given by the chain-dashed line in Figure 7.

### C. Comparison between Theoretical and Experimental \(k\), Rate Constants

There have been two experimental measurements of the temperature dependence of \(k_i\) which can be compared with the above theoretical analysis. In early work by Sridharan et al.,\(^3\)

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Reaction between OH and H₂O

The calculated temperature dependence of $k_1$ determined here (see Figure 7) can be combined with the average rate constant for all experimental measurements at 298 K ($=8.6 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) to obtain a “best” estimate of the absolute value and temperature variation of $k_1$:

$$k_1 = 7.1 \times 10^{-11} (T/300)^{0.21} \exp(113/RT)$$

Evaluating this rate expression at 1100 K gives a value of $5.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ in excellent agreement with the recent measurement of Hippler et al.38 (i.e., $5.0 \times 10^{-11}$) but significantly larger than earlier high-temperature measurements of $k_1$ (see Figure 7). We believe that this new rate expression is that preferred for modeling high-temperature combustion systems. At 1700 K, this value of $k_1$ is a factor of 7 larger than that used in the simulations of ref 45. The effect of this new value of $k_1$ on the simulated OH profile is shown in Figure 8. Individual points in this figure represent experimental data,45 and the dotted curve is obtained using the above value of $k_1$ with the other rate constants from Table I of ref 45. Evidently, changing the value of $k_1$ produces a significantly steeper OH decay profile and a poorer fit to the data.

Since the publication of ref 45, a new measurement of the temperature dependence of $k_1$ has become available46 in both N₂ and H₂O diluents. The value of this rate constant in the burned gas mixture at 1700 K is approximately 35% smaller than that used previously,45 primarily because of a reduction in the measured collision efficiency of H₂O relative to N₂ at higher temperature. Therefore, we have carried out a new fit to the OH decay curve in the lean flame using the rate constants of ref 45 with the exception that $k(\text{OH} + \text{H}_2\text{O})$ was changed to expression $k_1$ above and $k(\text{H} + \text{O}_2 + \text{N}_2) = 6.5 \times 10^{-32} \exp(1350/RT)$ was used.46 The collision efficiency for H₂O at 1700 K was determined to be 3.66,46 and that of CO₂ was estimated to be 2.0. All other efficiencies were set equal to that of N₂ (=1.0). No data are available for the CO₂ collision efficiency, but it is likely that it is somewhat larger than N₂ and smaller than H₂O. A value of 1.0 for CO₂ would, in fact produce an imperceptible change in the quality of the fit. The solid line in Figure 8 is the fit obtained using these new rate constants and collision efficiencies. The agreement with the experimental data is excellent.

IV. Discussion

A. Triplet Electronic Structure Calculations. One of the most interesting aspects of the OH + H₂O reaction is the relationship between the planar potential energy surfaces for the $3^A''$ and $3^A'$ electronic states and the two nonplanar $3^A$ potential surfaces, which originate from these planar surfaces. The ground-state products H₂O and CO₂ correlate with the $3^A''$ state. However,

$$H + O_2 + M = H_2O + M \quad (9)$$

in the combustion of fuel-lean mixtures as has been demonstrated by a comparison of computer-simulated OH profiles to those measured experimentally in propane-air flames.43 The OH density immediately beyond the flame zone in the fuel-lean flame ($\phi = 0.63$) described in this reference is far above thermal equilibrium and decreases in the burned gas toward equilibrium over a distance of several millimeters. The shape of the OH decay profile is controlled in large part by the formation and subsequent
since the $3A'$ hydrogen-bonded complex HO$^+$$HO_2$ has a potential energy $\sim$4 kcal/mol lower than that for the $3A''$ complex (see Tables III and IV), the ground-state nonplanar potential energy surface initially followed by the reactants correlates with the $3A'$ surface. At shorter reactant separations the $3A''$ and $3A'$ surfaces cross, which becomes an avoided crossing in nonplanar configurations. As shown in Figures 4 and 5 there are two different general locations for this crossing.

In the calculations presented here the structure of the nonplanar $3A$ transition state, which correlates with the $3A''$ transition state, is determined. Though calculations of energies and optimized structures at the HG/6-31G** level and the MP2/6-31G** level indicate that the $3A''$-$3A'$ crossing is that depicted in Figures 4a and 5a, it is not felt that the calculations reported here are sufficiently accurate to rule out the possibility that the crossing in Figures 4b and 5b is correct. For example, calculations with MP2/6-31G** optimized geometries and HF/6-31G* energies give the crossing in Figures 4b and 5b. We feel that multireference CI calculations may be needed to establish the definitive nature of the $3A''$-$3A'$ crossing.

The size and temperature dependence of the experimental rate constant for reaction 1 indicate that the rate control is determined by the long-range OH $+$$HO_2$ attractive potential.2 The nonplanar $3A$ transition state found here is much "too tight" to be consistent with the experimental factor. Thus, for passage of this transition state to not be rate controlling, the transition state's potential energy must be substantially less than that of the reactants. However, the nonplanar $3A$ transition state found in this work has a PM3 potential energy 1.5 kcal/mol higher than that of the reactants. If this is the proper transition state for the ground-state $3A$ surface, its potential energy must be lowered by 3.3 kcal/mol to be consistent with the experimental rate constant. However, as discussed above, this $3A$ transition state is the reaction transition state only if the $3A''$-$3A'$ crossing occurs before the $3A''$ transition state (Figure 4). If the actual crossing occurs after the $3A'$ transition state, the true $3A$ reaction transition state will differ from the $3A$ transition state found here and should have a lower potential energy, in better agreement with the experimental rate constants for the triplet surface. Since the rates for the OH $+$$HO_2$ $\rightarrow$$H_2O_3^*$ reaction on the singlet surface and the OH $+$$HO_2$ $\rightarrow$$H_2O_2$$+$$O_2$ reaction on the triplet surface are both controlled by the reactants long-range dipole–dipole potential, the ratio of $H_2O_3^*$ to $H_2O_2$$+$$O_2$ formation is predicted to be given by the electronic state degeneracies and is $1/3$. Therefore, if the bath gas pressure is increased to stabilize $H_2O_3^*$, the rate constant for the loss of OH would increase by 33%.

The above theoretical model can be compared with the experimental study of Dransfeld and Wagner.35 They studied the $16O^+$$H_16O_2$ reactive system at room temperature and low pressures and found equal rates (within statistical uncertainties) for

\begin{align}
16OH & + H_16O_2 \rightarrow H_2O^+ + 16O_2 \\
16OH & + H^+O_2 \rightarrow 16OH + H^+O_2
\end{align}

The ab initio calculations reported here and in ref 18 indicate reaction 10a occurs on the triplet surface and reaction 10b occurs on the singlet surface by trioxide formation and ensuing decomposition, with one-half of the trioxide decomposing by reaction 10b. Therefore, the result of Dransfeld and Wagner35 indicates that the rate of OH $+$$HO_2$ association on the singlet surface to form $H_2O_3^*$ is twice the rate of OH $+$$HO_2$ $\rightarrow$$H_2O_2$$+$$O_2$ on the triplet surface. This differs significantly from our prediction that the rate of $H_2O_2$$+$$O_2$ formation to $H_2O_3^*$ formation is 3/1.

An explanation of the above difference is not obvious. As discussed before,32 impurities in the experimental reaction system may have affected the experimental findings. It is also possible that the electronic adiabatic model we have assumed for the singlet and triplet surfaces should be modified. In this model it is assumed that the singlet and triplet reactions only occur on the ground-state $3A'$ and $3A$ surfaces, respectively. It is possible that spin-allowed electronic transitions between the ground and excited $3A$ states and the ground and excited $3A'$ states should be included. In addition, dynamical effects (see the following) may be important.

Because of a basic assumption in our theoretical model, the theoretical rate constant for the triplet surface may be too large at high temperatures. The theoretical model for the rate constant is based on the reactant long-range dipole–dipole potential in eq 4. This potential does not differentiate between the two reactant orientations HO$^-$HO$_2$ and HO$_2$-HO. The former leads directly to products without an overall potential energy barrier, while the latter encounters a repulsive potential barrier at small separations. However, the theoretical expression for $k_1(T)$, eq 5, is based on the assumption that both orientations form products.32 As the temperature is increased there is less time for an unfavorable orientation to reorient as the reactants interact. However, this effect might be compensated by the increased reactant angular velocities at high temperatures. Nevertheless, eq 5 may overestimate $k_1(T)$ by up to a factor of 2 at high temperatures. It would be interesting to study reaction 1 by classical trajectory calculations.47

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Registry No. HO$_2$, 3170-83-0; OH, 3352-57-6.