The CH₃ + HO₂ Reaction: First-Principles Prediction of Its Rate Constant and Product Branching Probabilities

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The reaction of the CH₃ radical with HO₂ has been investigated by means of ab initio molecular orbital theory and variational RRKM theory calculations. The reaction can take place by several product channels producing (a) CH₄ + O₂ (\(^3\Sigma_g^-\)) and (b) CH₂ + O₂ (\(^\Delta\)) by direct H abstraction and (c) CH₃O + OH and (d) CH₂O + H₂O by an association/decomposition mechanism via CH₃OOH. The bimolecular reaction rate constants for the formation of these products have been calculated for the temperature range 300–3000 K and found to be pressure independent up to 50 atm. The Arrhenius equations for the two major channels a and c were found to be strongly curved; they can be represented by \(k_a = 4.23 \times 10^{-16} T^{2.25} \exp(828/T)\) for 300–800 K, \(k_c = 3.02 \times 10^{-21} T^{2.83} \exp(1877/T)\) for 800–3000 K, and \(k_c = 2.97 \times 10^{-10} T^{-0.34} \exp(182/T)\) for 300–1000 K and 1.02 \(\times 10^{-13} T^{0.76} \exp(1195/T)\) for 1000–3000 K, in units of cm³ molecule⁻¹ s⁻¹. In the abstraction channel a, the effect of multiple reflections above its van der Waals complex (CH₃•••HO₂), which lies 1.9 kcal/mol below the reactants with a 1.2 kcal/mol barrier leading to the formation of the CH₄ + O₂ (\(^3\Sigma_g^-\)) products, was found to be quite significant at low temperatures (\(T < 300 K\)). In addition, the predicted rate constant for the unimolecular decomposition of CH₃OOH agrees closely with the available experimental data using the heats of formation of CH₃O (5.4 ± 0.5 kcal/mol) and CH₃OOH (−29.0 ± 1.0 kcal/mol) calculated with the isodesmic method at 0 K.

1. Introduction

The reaction of CH₃ with HO₂ plays a pivotal role in the combustion of small hydrocarbons, particularly under moderate temperature (<1700 K) and high-pressure (>40 atm) conditions. The reaction has been shown to be highly influential on the evaluation of the CH₃ + O₂ reaction rate constant, because of the strong kinetic coupling in the complex chemistry of the CH₄ + O₂ oxidation reaction.

The kinetics for the CH₃ + HO₂ reaction has not yet been reliably determined experimentally because, in part, of the high degree of difficulty in measuring the concentrations of both radical reactants accurately for rate constant determination. The reaction is highly exothermic and it can conceivably take place via several product channels by the direct and indirect bimolecular reaction mechanisms as shown below:

The direct abstraction channels:

\[
\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2 \left( ^3\Sigma_g^- \right) \quad (a)
\]

\[
\rightarrow \text{CH}_2 + \text{O}_2 \left( ^\Delta \right) \quad (b)
\]

The association/decomposition channels:

\[
\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH}^\dagger \rightarrow \text{CH}_3\text{O} + \text{OH} \quad (c)
\]

\[
\rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad (d)
\]

\[
\rightarrow \text{CH}_3\text{OOH} \left( ^+_M \right) \quad (e)
\]

where the \(\dagger\) represents internal excitation. Among these elementary reaction steps; only the thermal decomposition of methylhydroperoxide (CH₃OOH) associated with step c has been studied experimentally. The exothermicities for the formation of these products can be found in Table 1 (vide infra). For a reliable prediction of the total rate constant and product branching probabilities under chemically activated conditions, a full characterization of the potential energy surfaces (PESs) involving both mechanisms is essential.

In this study, we calculate the PES of the whole system with the G2M method and estimate the rate constants for individual product channels employing transition-state theory (TST) for the direct abstraction process and the variational Rice–Ramsperger–Kassel–Marcus (RRKM) theory for the indirect bimolecular reaction via CH₃OOH. These computational methods will be presented in detail below.

2. Computational Methods

Ab Initio Calculations. The geometry of the reactants, intermediates, transition states, and products of the CH₃ + HO₂ reaction were optimized at the B3LYP/6-311G(d,p) level with Becke’s three-parameter nonlocal exchange functional with nonlocal correlation functional of Lee et al. The energies of all species were calculated by the G2M method, which uses a series of calculations with B3LYP/6-311G(d,p) optimized geometries to approximate the CCSD(T)/6-311+G(3df,2p) level of theory, including a “higher level correction” (HLC) based on the number of paired and unpaired electrons. The total G2M energy with zero-point energy (ZPE) correction is calculated as follows:

\[E(G2M[RCC, MP2]) = E(RCCSD(T)/6-311G(d,p)) + \Delta E(+3df, 2p) + \Delta E(HLC) + ZPE[B3LYP/6-311G(d,p)]\]
energies; was used to represent the potential energy along the individual
which solves the master equation 18

\[ E(HLC) = -0.005 25n_\text{e} - 0.000 19n_\text{a} \]

where \( n_\text{e} \) and \( n_\text{a} \) are the numbers of valence electrons, \( n_\text{e} \geq n_\text{a} \). All calculations were carried out with Gaussian 9816 and MOLPRO 9617 programs.

**Rate Constant Calculations.** The rate constants were computed with a microcanonical variational RRKM methods18–20 which solves the master equation18–23 involving multistep vibrational energy transfers for the excited intermediate (CH3O:H). The PES calculated at the G2M level, to be discussed in the next section, was used in the calculation.

Similar to our previous calculations24–27 with the Variflex code,18 the component rates were evaluated at the EJ-resolved level. The effect of pressure was studied by 1-D master equation calculations using the Boltzmann probability of the complex for the J distribution. The master equation was solved by an inversion based approach.18–20 To achieve convergence in the integration over the energy range, an energy grain size of 100 cm⁻¹ was used; this grain size provides numerically converged results for all temperatures studies with the energy spanning range from 15 000 cm⁻¹ below to 64 900 cm⁻¹ above the threshold. The total angular momentum \( J \) covered the range from 1 to 241 in steps of 10 for the EJ-resolved calculation. For the barrierless transition states, the Van der Waals potential20

\[ V(R) = D_\text{v} \left( 1 - \alpha \exp(-\beta (R^2 - R_0^2)) \right)^2 - D_\text{e} \]

was used to represent the potential energy along the individual reaction coordinate. In the above equation, \( D_\text{v} \) is the bond energy of CH₃-O₂ or CH₃-OH, excluding zero-point vibrational energies; \( \alpha = R_\text{e}/R_0 \), where \( R \) is the reaction coordinate (i.e., the distance between the two bonding atoms, in the present case C–O, or O–O), and \( R_0 \) is the equilibrium value of \( R \). For the tight transition states, the numbers of states were evaluated according to the rigid-rotor harmonic-oscillator approximation.

**3. Results and Discussion**

**A. Potential-Energy Surface and Reaction Mechanism.**

The optimized geometries of the reactants, intermediates, transition states, and products are shown in Figure 1; the potential energy diagram obtained at the G2M level is presented in Figure 2; the total and relative energies are compiled in Table 1; and the vibrational frequencies and moments of inertia of all species used in RRKM calculations are summarized in Table 2. As illustrated in Figure 2, the CH₃ + HO₂ reaction can occur via several product channels as alluded to before.

**H-Atom Abstraction Reaction.** As shown in Figure 2, the H-abstraction reaction can take place through a triplet PES via a van der Waals complex, vdW, with \( C_1 \) symmetry. The complex is more stable than the CH₃ + HO₂ reagents by 1.9 kcal/mol at the G2M level; it fragments readily via TS2 with a small (1.2 kcal/mol) barrier to give CH₄ and the ground-state molecule O₂ (\(^3\Sigma_g^-\)) with an overall exothermicity of 58.2 kcal/mol. From Figure 1, one can see that the C–H–O bond angle in TS2 is about 14° larger than that in vdW and the newly forming C–H bond length decreases from 2.159 Å in vdW to 1.45 Å in TS2. For both vdW and TS2, the O₂ and the C atom of the CH₃ radical are in the same plane. The CH₃ can also directly abstract the H atom from HO₂ through a singlet surface via TS3 to produce CH₄ and the excited O₂ (\(^1\Delta\)) molecule. The barrier and exothermicity of this channel are 4.1
O₂ from CH₃OOH unimolecularly failed to locate its transition state.

The CH₃ - HO₂ system computed at the G2M level.

and 29.4 kcal/mol, respectively. It is worth noting that an extensive search for an analogous path producing the excited O₂ was unsuccessful. It is worth noting that an additional path producing the excited O₂ was unsuccessful. It is worth noting that an additional path producing the excited O₂ was unsuccessful. It is worth noting that an additional path producing the excited O₂ was unsuccessful. It is worth noting that an additional path producing the excited O₂ was unsuccessful.

**Association/Decomposition Channels.** The association reaction of CH₃ + HO₂ by a barrierless process forms methylhydroperoxide, CH₃OOH, which has C₁ symmetry with 121.9° dihedral angle C—O—O—H, CH₃OOH lies 70.5 kcal/mol below the reactants at the G2M level. A further discussion on the heat of the formation of the peroxide molecule will be made later in conjunction with its thermal unimolecular decomposition reaction.

The internally excited CH₃OOH can dissociate via TS1 producing CH₃O + H₂O by a concerted H-migration/H₂O-elimination mechanism. No experimental data are available for this channel, although it is the most exothermic process with the exothermicity of 126.1 kcal/mol. To our knowledge, this calculation represents the first ab initio study on the reaction of CH₃ + HO₂ by a barrierless process forms methylhydroperoxide, CH₃OOH, which has C₁ symmetry with 121.9° dihedral angle C—O—O—H, CH₃OOH lies 70.5 kcal/mol below the reactants at the G2M level. A further discussion on the heat of the formation of the peroxide molecule will be made later in conjunction with its thermal unimolecular decomposition reaction.

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The energies used in the calculation are plotted in Figure 2, and the vibrational frequencies and moments of inertia are listed in Table 2. The LJ parameters required for the RRKM calculation of the unimolecular decomposition of CH₃OOH are approximated to be the same as those of CH₃OH (ε = 385.2 K and σ = 3.657 Å).

**H-Abstraction Reactions.** As mentioned in the previous section, the H atom of HO₂ can be abstracted by the CH₃ radical via the triplet or singlet surface to produce CH₃O and O₂ (1Δ), respectively. The formation of O₂ (1Δ) by channel a takes place by the vdW. Our calculated results show that, at high temperatures, the rate constant is mainly controlled by the transition state (TS2) connecting the vdW and the CH₃ + O₂ (1Δ) products. We have examined the effect of multiple reflections above the well of the vdW complex using the method of Hirschfelder and Wigner as discussed by Miller. The effect was found to be <1% at high temperatures (>2000 K); however, it becomes much stronger at low temperatures (T < 300 K) as illustrated in Figure 3. The predicted rate constant shown in Figure 3 reveals a weak negative temperature dependence below 800 K and a small positive temperature dependence above 800 K. The predicted result agrees reasonably with the value estimated by Tsang and Hampson (see Figure 3).

The formation of O₂ (1Δ) by channel b proceeds directly via TS3 with 4.1 kcal/mol barrier. The rate constant (kₗ) has a positive temperature dependence between 300 and 3000 K and is much smaller than kₗ because of the higher barrier. It should be pointed out that the lowest vibrational modes, 17 cm⁻¹ in TS2 and 59 cm⁻¹ in TS3, were treated as classical one-dimensional free rotors in our rate constant calculations. These rate constants in the 300–3000 K range can be represented by the expressions in units of cm³ molecule⁻¹ s⁻¹:

\[
  k_a = 4.23 \times 10^{-16} \exp(828/T), \quad 300-800 \text{ K}
\]

\[
  k_b = 8.76 \times 10^{-17} \exp(-1181/T), \quad 300-3000 \text{ K}
\]

**Bimolecular Association/Decomposition Reactions.** As aforementioned, the association reaction of CH₃ with HO₂ producing methylhydroperoxide occurs without a well-defined transition state because of the absence of a reaction barrier. To reliably predict the association rate, the flexible variational transition state approach originally developed by Marcus and co-workers has been employed by means of the Variflex code as alluded to above. The association potential energy surface for the approach of CH₃ to HO₂ forming CH₃OOH was calculated by varying the forming C—O bond distance from 3.4 Å to its equilibrium value, 1.4163 Å, with an interval of 0.1 Å. Other geometric parameters were fully optimized with the C—O—O—H dihedral angle fixed at 121.9° for each C—O separation at the B3LYP/6-31G(d,p) level of theory. For each structure, we calculated the 3N-7 vibrational frequencies, projected out of the gradient direction. The B3LYP-calculated total energies at each point were fitted by a Varshni potential energy function:

\[
  E_T = E_0 + \frac{1}{2} k (T - T_0)^2
\]

where E₀ = 1.4163 Å, with an interval of 0.1 Å. Other geometric parameters were fully optimized with the C—O—O—H dihedral angle fixed at 121.9° for each C—O separation at the B3LYP/6-31G(d,p) level of theory. For each structure, we calculated the 3N-7 vibrational frequencies, projected out of the gradient direction. The B3LYP-calculated total energies at each point were fitted by a Varshni potential energy function:

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\[
  E_T = E_0 + \frac{1}{2} k (T - T_0)^2
\]
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Unimolecular Decomposition of CH₃OOH. The unimolecular decomposition of CH₃OOH is the only process which has been experimentally measured. 8,9,36,37 The theoretically predicted dissociation rate constants for the decomposition reaction CH₃OOH → CH₃ O + OH at 25 Torr and 1 atm in temperature range of 400–1000 K in N₂ are compared with available experimental data in Figure 5a,b. The solid and dotted lines given in the figures represent the calculated results in which the heat of

TABLE 2: Vibrational Frequencies and Moments of Inertia Used in Rate Constant Calculations for the Main Species of the CH₃ + HO₂ Reaction at the B3LYP/6-311G(d,p) Level of Theory

<table>
<thead>
<tr>
<th>species</th>
<th>$I_i$ (au)</th>
<th>frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>6.3, 6.3, 12.6</td>
<td>504, 1403, 1403, 3105, 3284, 3284</td>
</tr>
<tr>
<td>HO₂</td>
<td>2.9, 53.6, 56.5</td>
<td>1162, 1427, 3610</td>
</tr>
<tr>
<td>CH₃O</td>
<td>6.3, 46.2, 52.6</td>
<td>1202, 1270, 1539, 1827, 2868, 2917</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>11.4, 64.6, 65.0</td>
<td>710, 963, 1108, 1360, 1371, 1518, 2890, 2955, 2995</td>
</tr>
<tr>
<td>OH</td>
<td>3.2, 3.2</td>
<td>3704</td>
</tr>
<tr>
<td>CH₃OOH</td>
<td>41.6,173.3,198.9</td>
<td>143, 252, 446, 876, 1037, 1171, 1205, 1372, 1451, 1547, 1512 3002, 3107, 3107, 3777</td>
</tr>
<tr>
<td>vDW</td>
<td>57.6, 380.2,1425.3</td>
<td>96, 106, 142, 147, 289, 415, 649, 1271, 1448, 1454, 1495, 3155, 3345, 3535, 3579</td>
</tr>
<tr>
<td>TS1</td>
<td>54.9, 183.8, 226.1</td>
<td>1544, 204, 472, 509, 631, 1069, 1091, 1230, 1244, 1287, 1516, 1789, 2946, 3037, 3610</td>
</tr>
<tr>
<td>TS2</td>
<td>38.6, 349.6, 374.5</td>
<td>542, 17, 170.0, 268, 373, 476, 1008, 1428, 1446, 1484, 1854, 3056, 3078, 3194, 3221</td>
</tr>
<tr>
<td>TS3</td>
<td>47.9, 304.7, 340.4</td>
<td>2111, 59, 150.0, 382, 509, 618, 1006, 1134, 1447, 1451, 1452, 1530, 3128, 3299, 3305</td>
</tr>
</tbody>
</table>

TABLE 3: Heat Formation of CH₃OOH Calculated by the Isodemic Method at the G2M Level

<table>
<thead>
<tr>
<th>reaction</th>
<th>$\Delta H^0$ (0K)</th>
<th>$\Delta H^0$ (CH₃OOH, 0K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH + NO₂ → CH₃OOH + NO</td>
<td>29.8</td>
<td>-28.5 ± 0.3</td>
</tr>
<tr>
<td>CH₃O + HOOH → CH₃OOH + OH</td>
<td>4.8</td>
<td>-30.0 ± 0.21</td>
</tr>
<tr>
<td>CH₃ + HOOH → CH₃OOH + H</td>
<td>17.1</td>
<td>-29.9 ± 0.18</td>
</tr>
<tr>
<td>CH₃OH + HOOH → CH₃OOH + H₂O</td>
<td>-8.8</td>
<td>-28.0 ± 0.13</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td>-29.0 ± 1.0</td>
</tr>
</tbody>
</table>

* Values are in units of kcal/mol. The heats of formation reference species at 0 K were taken from ref 39, except that of CH₃O from ref 26. The errors given in the calculated values convolute all reported experimental ones.

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The CH$_3$ + HO$_2$ Reaction

The heat of formation of CH$_3$O gives slightly small decomposition formation of CH$_3$O at 0 K was taken to be 5.4 and 6.8 kcal/mol, based on our recent isodemic calculations and on the experimental value of Neumark and co-workers. The high-pressure limit rate constants for CH$_3$OOH Decomposition at 100 Torr; 1, 10, and 50 atm, and the High Pressure Limit in N$_2$ in Units of s$^{-1}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>100 Torr</th>
<th>1 atm</th>
<th>10 atm</th>
<th>50 atm</th>
<th>high pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>$3.12 \times 10^{-9}$</td>
<td>$5.51 \times 10^{-9}$</td>
<td>$7.14 \times 10^{-9}$</td>
<td>$7.51 \times 10^{-9}$</td>
<td>$7.63 \times 10^{-9}$</td>
</tr>
<tr>
<td>500</td>
<td>$5.22 \times 10^{-9}$</td>
<td>$7.56 \times 10^{-9}$</td>
<td>$1.2 \times 10^{-8}$</td>
<td>$1.20 \times 10^{-8}$</td>
<td>$1.70 \times 10^{-8}$</td>
</tr>
<tr>
<td>600</td>
<td>$9.19 \times 10^{-9}$</td>
<td>$1.16 \times 10^{-8}$</td>
<td>$1.27 \times 10^{-8}$</td>
<td>$2.65 \times 10^{-8}$</td>
<td>$2.95 \times 10^{-8}$</td>
</tr>
<tr>
<td>700</td>
<td>$1.10 \times 10^{-8}$</td>
<td>$2.84 \times 10^{-9}$</td>
<td>$3.81 \times 10^{-9}$</td>
<td>$7.25 \times 10^{-9}$</td>
<td>$8.58 \times 10^{-9}$</td>
</tr>
<tr>
<td>800</td>
<td>$7.65 \times 10^{-9}$</td>
<td>$2.17 \times 10^{-9}$</td>
<td>$3.13 \times 10^{-9}$</td>
<td>$5.53 \times 10^{-9}$</td>
<td>$7.25 \times 10^{-9}$</td>
</tr>
<tr>
<td>900</td>
<td>$2.25 \times 10^{-9}$</td>
<td>$4.50 \times 10^{-9}$</td>
<td>$6.66 \times 10^{-9}$</td>
<td>$1.11 \times 10^{-8}$</td>
<td>$1.40 \times 10^{-8}$</td>
</tr>
<tr>
<td>1000</td>
<td>$1.27 \times 10^{-8}$</td>
<td>$5.93 \times 10^{-9}$</td>
<td>$8.77 \times 10^{-9}$</td>
<td>$1.80 \times 10^{-8}$</td>
<td>$2.19 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

by

$k_c^e = 2.22 \times 10^{7} T^{-0.42} \exp(-22 457/T) \text{ s}^{-1}$ (25 Torr)

$k_c^e = 3.09 \times 10^{2} T^{4.51} \exp(-20 009/T) \text{ s}^{-1}$ (1 atm)

covering the temperature range 400–1000 K. Table 4 summarizes the theoretically predicted decomposition rate constants of CH$_3$OOH at different N$_2$ pressures in the temperature range of 400–1000 K.

4. Conclusion

The reaction of CH$_3$ with HO$_2$ has been studied in detail by ab initio MO and statistical theory calculations. The reaction can occur by several paths through the direct abstraction of H from HO$_2$ by CH$_3$ and the indirect association/decomposition process via CH$_3$OOH, producing CH$_3$O + OH and CH$_3$O + H$_2$O. The direct abstraction reaction producing CH$_4$ and O$_2$ may occur via a triplet or singlet PES giving rise to the molecular oxygen in its ground electronic state ($\Sigma^+_g$) or excited $^1\Delta$ state, respectively. The reaction over the triplet surface proceeds via a van der Waals complex with a 1.9 kcal/mol binding energy and a small (1.2 kcal/mol) barrier leading to the CH$_4$ + O$_2$ products. We have examined the effect of multiple reflections above the complex on the predicted rate constant; it was found to be quite significant at low temperatures ($T < 300$ K). The formation of O$_2$ ($^1\Delta$) has a 4.1 kcal/mol reaction barrier.
rate constants for both processes have been calculated for combustion applications in the 300—3000 K temperature range.

The formation of CH$_3$OOH by the CH$_3$—O$_2$H association and the decomposition of the peroxide molecule producing CH$_3$O + OH both occur barrierlessly. Their transition states were characterized by the flexible transition-state approach with the Variflex code of Klippenstein and co-workers. The production of CH$_3$O from CH$_3$ + HO$_2$ dominates the reaction, and its rate constant was found to be at least 2 orders of magnitude greater than that for CH$_3$O formation despite the much larger exothermicity of the latter process. These two reactions were found to be pressure-independent up to 50 atm of N$_2$.

The rate constants for the thermal unimolecular decomposition of CH$_3$OOH have been calculated and compared with the available literature data obtained at 25 Torr and atmospheric pressure. The agreement was excellent if the heats of formation predicted by the isodesmic method for CH$_3$O and CH$_3$OOH, 5.4 ± 0.5 and −29.0 ± 1.0 kcal/mol, respectively, were employed in the calculation.

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**References and Notes**


