Insight into Selected Reactions in Low-Temperature Dimethyl Ether Combustion from Born–Oppenheimer Molecular Dynamics

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Dimethyl ether is under consideration as an alternative diesel fuel. Its combustion chemistry is as yet ill-characterized. Here we use Born–Oppenheimer molecular dynamics (BOMD) based on DFT-B3LYP forces to investigate the short-time dynamics of selected features of the low-temperature dimethyl ether (DME) oxidation potential energy surface. Along the chain propagation pathway, we run BOMD simulations from the transition state involving the decomposition of \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \) to two CH₃=O and an \( \cdot \text{O} \) radical. We predict that formaldehyde \( \text{C}–\text{O} \) stretch overtones are excited, consistent with laser photolysis experiments. We also predict that \( \text{O}–\text{H} \) overtones are excited for the \( \cdot \text{OH} \) formed from \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \) dissociation. We also investigate short-time dynamics involved in chain branching. First, we examine the isomerization transition state of \( \cdot \text{OOCH}_2\text{OCH}_2\text{OOH} \). The latter species is predicted to be a short-lived metastable radical that decomposes within 500 fs to hydroperoxymethyl formate (HPMF; \( \text{HOOCH}_2\text{OC}(=\text{O})\text{H} \)) and the first \( \cdot \text{OH} \) of chain branching. The dissociation of HOOCH₂OCHOH exhibits non-RRKM behavior in its lifetime profile, which may be due to conformational constraints or slow intramolecular vibrational energy transfer (IVR) from the nascent \( \cdot \text{H}–\text{O} \) bond to the opposite end of the radical, where \( \text{O}–\text{O} \) scission occurs to form HPMF and \( \cdot \text{OH} \). In a few trajectories, we see HOOCH₂OCHOH recross back to \( \cdot \text{OOCH}_2\text{OCH}_2\text{OOH} \) because the isomerization is endothermic, with only an 8 kcal/mol barrier to recrossing. Therefore, some inhibition of chain-branching may be due to recrossing. Second, trajectories run from the transition state leading to the direct decomposition of HPMF (an important source of the second \( \cdot \text{OH} \) radical in chain branching) to \( \text{HCO} \), \( \cdot \text{OH} \), and \( \text{HC}(=\text{O})\text{OH} \) show that these products can recombine to form many other possible products. These products include \( \text{CH}_2\text{OO} + \text{HC}(=\text{O})\text{OH} \), \( \text{H}_2\text{O} + \text{CO} + \text{HC}(=\text{O})\text{OH} \), \( \text{HC}(=\text{O})\text{OH} + \text{HC}(=\text{O})\text{OH} \), and \( \text{HC}(=\text{O})\text{C}(=\text{O})\text{H} + \text{H}_2\text{O} \), which (save \( \text{CH}_2\text{OO} + \text{HC}(=\text{O})\text{OH} \)) are all more thermodynamically stable than the original \( \text{HCO} + \cdot \text{OH} + \text{HC}(=\text{O})\text{OH} \) products. Moreover, the multitude of extra products suggest that standard statistical rate theories cannot completely describe the reaction kinetics of significantly oxygenated compounds such as HPMF. These secondary products consume the second \( \cdot \text{OH} \) required for explosive combustion, suggesting an inhibition of DME fuel combustion is likely.

I. Introduction

With ever more stringent restrictions being placed on the emissions of air pollutants such as \( \text{NO}_x \) and particulate matter around the world, the need for clean-burning alternative sources of energy becomes more pressing. Dimethyl ether (DME) has been proposed as a replacement for conventional diesel fuel. DME’s propensity to compression ignite is comparable to that of conventional diesel fuel, which is comprised of long-chain hydrocarbons. Unlike conventional diesel fuel, DME creates little soot when combusted at relatively low temperatures. This “soot-free” property has been attributed to DME’s lack of carbon–carbon bonds in its molecular structure, which inhibits soot aggregation. Dimethyl ether also has a number of other desirable properties such as low toxicity and low photoactivity. DME can also be produced economically in a single-step synthesis process, and current liquid petroleum gas (LPG) technology can form a basis for future DME storage and infrastructure. The mechanism for low-temperature autoignition has been modeled after analogous mechanisms for low-temperature oxidation of long-chain hydrocarbons. This mechanism involves chain branching, in which there is an exponential increase in the number of highly reactive radicals (e.g., \( \cdot \text{OH} \), \( \text{HOO}^* \), etc.). A basic schematic representation of DME’s primary low-temperature chain mechanism pathways based on our previous calculations is shown in Figure 1. Labeling of the transition state barriers follows the labeling scheme of our previous work. The mechanism begins with \( \text{O}_2 \) addition to \( \text{CH}_2\text{OCH}_2 \) radical, which has been formed via hydrogen abstraction from \( \text{CH}_2\text{OCH}_3 \) in the initiation step. The most probable species involved in hydrogen abstraction from \( \text{CH}_2\text{OCH}_3 \) are \( \text{O}_2 \) (initial oxidation), \( \text{HOO}^* \), and \( \cdot \text{O} \) (the most reactive). Two paths are represented in Figure 1: a chain propagation path in which one \( \cdot \text{OH} \) is formed and a chain-branching path in which two \( \cdot \text{OH} \) are formed. Chain-branching begins when \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \) is...
diverted from the propagation path via a collision with \( \text{O}_2 \) to form \( \cdot \text{OOCH}_2 \text{OCH}_2 \text{OOH} \). If \( \cdot \text{OOCH}_2 \text{OCH}_2 \text{OOH} \) does not dissociate back into its precursors, it can undergo reactions that ideally lead to the production of two highly reactive \( \cdot \text{OH} \) radicals.

As we have shown previously, \(^5\) the chain-branching intermediate hydroperoxymethyl formate (HOOCH\(_2\)OC(\(=\)O)H, HPMF) has several possible dissociation channels that do not necessarily lead to the formation of a second \( \cdot \text{OH} \) radical. For simplicity, Figure 1 shows only the four lowest energy reaction paths. The lowest energy path leads to the formation of a hydrogen-bonded complex of carbonyl oxide (the Criegee intermediate of ethylene ozonolysis) and formic acid. A second path shown in Figure 1 (in blue) leads to noncomplexed carbonyl oxide and formic acid. The Criegee intermediate can decompose into \( \cdot \text{OH} \) and other products unimolecularly\(^6\)–\(^15\) or bimolecularly.\(^16\)–\(^29\) The second lowest energy path is the formation of the radicals \( \cdot \text{OCH}_2 \text{OC(=O)H} \) and \( \cdot \text{OH} \) via scission of the O=O bond in HPMF. The fourth lowest energy path shown in Figure 1 directly leads to \( \cdot \text{OH} \) radical along with HCO and H(C(\(=\)O)-OH). The barrier to this reaction is comparable to that for producing noncomplexed carbonyl oxide and formic acid.\(^4\)\(^5\) Both direct \( \cdot \text{OH} \) and formic acid formation and noncomplexed \( \text{CH}_2\text{OO} \) and H(C(\(=\)O)-OH) formation are energetically\(^2\) and kinetically\(^30\) unfavorable compared with the O=O scission and \( \text{CH}_2\text{OO} \rightarrow \text{HCO} \) complex formation pathways.

Experimental data are sparse for low-temperature DME oxidation. The most thorough studies of the kinetics of the chain propagation pathway (black curve in Figure 1) were done by Sehested et al.\(^31\) and Maricq et al.\(^32\) Sehested et al. used indirect methods (smog chamber with detailed kinetics modeling) while Maricq et al. employed laser photolysis techniques to derive their respective kinetics data. Both studies were conducted in conditions below and around atmospheric (1 atm and 298 K). Since Maricq et al. performed their experiments in real time, they were able to observe a dynamical aspect of the dissociating \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \) radical. They noted that their rate of dissociating \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \) derived from observed formaldehyde formation was about two times lower than the rates determined indirectly through measuring \( \text{CH}_2\text{OOH} \) loss and \( \text{CH}_2\text{OCH}_2\text{OO} \) formation with time-resolved UV spectroscopy. They reasoned that \( \text{CH}_2=\text{O} \) was produced vibrationally excited due to the \( \sim 40 \text{ kcal/mol} \) excess energy from the reactants, \( \text{CH}_2\text{OCH}_3 + \text{O}_2 \). They measured \( \text{CH}_2=\text{O} \) formation with a diode laser that probed the \( \nu = 0 \rightarrow \nu = 1 \) transition of the \( \text{CH}_2=\text{O} \) carbonyl stretching mode. Thus, \( \text{CH}_2=\text{O} \) with a vibrationally excited C=O stretch would be “transparent” to their diode laser probe when formed from \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \). The excited \( \text{CH}_2=\text{O} \) would then relax via collisions and would be visible to the probe only at later times. The present work will provide theoretical evidence in support of this proposal.

Even less is known about the chain branching pathway. Experiments of Curran et al.\(^3,33\) Dagaut et al.,\(^34\) and Liu et al.\(^35\) represent the only experimental (with detailed kinetics modeling) studies addressing the low-temperature chain-branching mechanism of DME. The most thorough of these studies of the low-temperature chain-branching mechanism is that of Curran et al.\(^3,33\) These studies, however, only give direct information about stable product yields. Mechanistic details of DME combustion must be inferred from stable product yields within a comprehensive kinetics model. These studies do not explore possible dynamics issues that may occur in the low-temperature chain mechanism. Thus, the aim of the present work is to probe areas of the DME chain reaction mechanism potential energy surface where short-time dynamics may yield insight into behavior that cannot be predicted by standard statistical rate theories (e.g., conventional transition state theory (CTST) and RRKM theory).

As we shall see, the reaction dynamics we observe indicates a mechanistic complexity in the combustion of DME not anticipated from such statistical kinetics theories.
II. Theoretical Method

A. Electronic Structure Details. Absolute energies, optimized structures, and harmonic frequencies for the systems considered here were calculated in our previous work.\(^4,5\) Born–Oppenheimer molecular dynamics treats the motion of the nuclei classically with Newton’s equations. However, the light mass of hydrogen in general should not be treated with classical dynamics. Deuterium is typically heavy enough to be treated classically. Therefore, to minimize the error in the classical dynamics used to propagate the nuclei due to neglecting quantum effects of light hydrogens, we have replaced all hydrogens with deuterium. Though good direct dynamics results have been attained for direct reactions of hydrogenated $\text{H} + \text{H}_2$ and hydrogenated trimethylene, $\text{H} + \text{H}_2$ is much smaller than our systems, which have 24–30 degrees of freedom, and the primary focus of Doubleday and co-workers’ trimethylene work was to determine branching ratios of the conrotatory and disrotatory rotation of the methylene ends formed in cyclopropane ring-breaking. Most of our systems involve hydrogen transfer between heavy carbon and oxygen atoms, which occurs either directly from the transition state or indirectly later on in the trajectory. Zero-point energy flow is a problem for high frequency $\text{O}–\text{H}$ and $\text{C}–\text{H}$ stretches, hence our use of deuterium instead of hydrogen. Our results may be viewed as only qualitatively correct for hydrogenated species and as predictions for deuterated experiments that may one day be performed. Though deuterium was used in all molecular dynamics simulations presented here, hydrogen atom notation is used in all chemical formulas to prevent confusion.

These calculations were performed using spin-polarized (unrestricted, U) density functional theory (DFT) employing the B3LYP hybrid exchange-correlation functional\(^{40}\) with the 6-31G** basis set\(^{41,42,43}\) within the Jaguar ab initio code.\(^{44}\) Though geometries are available from our previous work using a larger 6-311G** basis set (which may more accurately portray the thermochemistry),\(^{45}\) running trajectories with 10–12 atoms with the larger basis set would be computationally prohibitive. Thus, all single-point energy/gradient calculations for each molecular dynamics time step were computed at the DFT-B3LYP/6-31G** level of theory. Tables comparing our previous 6-31G** and 6-311G** results may be found in our earlier work.\(^4,5\) The Hessian (energy second derivative matrix) eigenvalues and eigenvectors from a subsequent harmonic frequency analysis were extracted to select initial conditions for the molecular dynamics trajectories, which will be discussed in the next section.

Spin contamination in unrestricted DFT is considerably less than in other unrestricted electronic structure methods, such as unrestricted Hartree–Fock (HF) and unrestricted Möller–Plesset perturbation theory (e.g., MP2, MP4). For the open-shelled systems considered in this study, the highest spin contamination was seen for the p-TS2 transition state. Instead of $\langle S^2 \rangle = 0.75$ for a pure doublet system, we find a value of 0.773 for p-TS2 (3% spin contamination). DFT’s lower spin contamination with respect to unrestricted wave function-based theories is a consequence of electron correlation being incorporated through the exchange-correlation functional. Pople and co-workers have asserted that “spin contamination” is not even well-defined for DFT.\(^{46}\) DFT’s formalism is laid out in terms of a density and not a wave function, and Pople et al. argue that real systems can display spin polarization. Moreover, bond dissociation is often well described by UDFT. For example, the $\text{O}–\text{H}$ bond dissociation of water, where $\text{H}_2\text{O}$ goes from a singlet species to two doublet species ($^{1}\text{H}^*$ and $^{1}\text{OH}$) is well-described by UDFT-B3LYP and does almost as well as the multireference complete active space SCF (CASSCF) level of theory.\(^{47}\)

The mean average error in the thermochemistry of DFT-B3LYP has been reported to be 3-5 kcal/mol.\(^{48,47}\) However, this mean average error covers standard systems where experimental heats of formation are well-known (e.g., $\text{H}_2\text{O, C}_2\text{H}_6$). By contrast, only some bond energies of peroxo radical and peroxide species (HO, HOH, $\text{CH}_3\text{OOH, CH}_2\text{CH}_2\text{OOH}$, and $\text{CH}_3\text{CH}_2\text{OO}$) have been measured; in these cases, we have found that the error is higher, with a mean average error of 5–9 kcal/mol depending on the system and basis set.\(^49\) Furthermore, we have found in the analogous ethyl radical + $\text{O}_2$ system, that the mean error with respect to known experimental thermochemistry derived from kinetics data is 6–7 kcal/mol.\(^{50}\) One might then suggest that a “more accurate” ab initio theory should be employed. In both the peroxo radical/peroxide bond energies and the ethyl + $\text{O}_2$ studies, the corresponding coupled cluster with single, double, and perturbative triple excitations (CCSD(T))\(^{50}\) results have average errors only 0.2–1 kcal/mol more accurate than those of DFT-B3LYP. Thus, there is little accuracy gain in applying the much more computationally demanding CCSD(T) method over the DFT-B3LYP method. The only methods that claim to attain chemical accuracy (i.e., 1–2 kcal/mol) are the Gaussian-2 (G2)\(^{51}\) and the complete basis set (CBS)\(^52\) methods. These are heuristic methods comprised of additive terms from a number of ab initio methods (e.g., HF, MP2, QCISD(T)). G2 and CBS only calculate the single-point energy of a given system and rely on the optimized geometries from other methods such as HF, MP2, and DFT-B3LYP. Therefore, G2 and CBS do not calculate gradients and cannot be used in BOMD to calculate forces on the nuclei. Therefore, we concluded that DFT-B3LYP is the best option currently available for use in BOMD simulations.

B. Molecular Dynamics Initial Conditions. The Hessian information from electronic structure calculations mentioned above was used in a subsequent random selection of momenta and positions calculated with a code written in our group implementing the quasiclassical normal mode sampling developed by Hase and co-workers.\(^{53,54}\) In this method, the system is treated as an ensemble of harmonic oscillators, and energy is distributed among the normal modes. Each normal mode is given energy based on a suitable probability distribution. In this work, we selected the energy for each normal mode according to the harmonic quantum Boltzmann distribution $P_i = \exp(-\hbar v_i / k_B T)\exp(-\hbar v_i / k_B T), where$ $n_i$ is the number of quanta of the $i$th mode, $h$ is Planck’s constant, $v_i$ is the frequency of the $i$th mode (computed from the Hessian eigenvalues), $k_B$ is Boltzmann’s constant, and $T$ is the temperature.\(^{55}\) Due to the locally high barriers along the combustion pathway, all trajectories were started from transition state structures so that rare event dynamics could be studied. The momentum selected along the reaction coordinate is chosen at random using $p_{rc} = \pm\sqrt{-2k_B T \ln(1-R)^{1/2}},$ where $R$ is a uniform random number.\(^{56}\) The Hessian eigenvector matrix is used to make the necessary transformation from internal to Cartesian coordinates and momenta. For finite displacements, the harmonic normal mode approximation is not exact; thus, the selected nuclear velocities and coordinates are rescaled to the desired energy (within 0.1%).\(^{57}\) The angular momentum of the system was set to $J = 0$ for all trajectories. Spurious angular momentum was removed iteratively with the rescaling of the energy prior to initiating each trajectory. Though selection of angular momentum according to a thermal distribution may be important in modeling possible Coriolis effects,\(^{57}\) the angular momentum of all
trajectories was set to \( J = 0 \) for simplicity. The effects of angular momentum are expected to be small compared to that of the internal vibrational energy. At 600 K, the equipartition theorem predicts an average classical total rotational energy of \( \frac{3}{2}RT = 1.8 \text{ kcal/mol} \), which is much smaller than the zero point and thermal vibrational energy of the 10 and 12 atom molecules considered here. Indeed, in ClONO (a much smaller system than those considered here) isomerization/dissociation molecular dynamics simulations, Peña-Gallego et al.\textsuperscript{58} found little change in rate constants and branching ratios when \( 1 \text{–} 2 \text{ kcal/mol} \) of rotational energy was added to any of the ClONO’s principal axes.

Temperatures for the selection of initial momenta and coordinates for each transition state were chosen based on whether the transition state belonged to the chain-propagation or the chain-branching mechanism. For chain-propagation transition states (p-TS2), a temperature of 300 K was chosen for initialization of the velocities and coordinates. This temperature is within the range of the experiments of Marić et al.\textsuperscript{32} (296–350 K); again, their study addresses dynamical aspects of formaldehyde and ‘OH production from \( \text{CH}_3\text{OCH}_2^+ + \text{O}_2 \). For transition states involved in chain branching (i.e., b-TS1, b-TS2, b-TS5, and b-TSS’), a temperature of 600 K was chosen. This temperature is in the range of peak low-temperature yield of the chain-branching product formaldehyde acid observed in the experiments of Liu et al.\textsuperscript{35} and Curran et al.\textsuperscript{33}

C. Trajectory Integration. The velocity–Verlet algorithm of Swope et al.\textsuperscript{59} was used to integrate Newton’s equations of motion for microcanonical (constant \( N, V, E \)) dynamics. The time step for all these calculations was 10 atomic time units (~0.242 fs). The duration of each trajectory varied, depending on which part of the potential surface we were considering. Trajectories from p-TS2, b-TS2, b-TS5, and b-TSS’ (see Figure 1), each ran for 1 ps. Ten trajectories were executed for the simulation of \( \text{CH}_3\text{OCH}_2\text{OCH}_2\text{OOH} \) dissociation from p-TS2, 30 trajectories for the dissociation of HPMF (deuterated) through b-TS2, and 10 each for the dissociation of HPMF (deuterated) through b-TSS’ and through b-TSS’. For the trajectories from b-TS1, a duration of 500 fs was determined from preliminary trajectories to be sufficient for the dissociation of HOOCH\(_2^\circ\)OCHOH. Then 70 trajectories were followed for the isomerization of ‘OOC\(_2\text{H}_2\text{OCH}_2\text{OOH} \) to HOOCH\(_2^\circ\)OCHOH through b-TS1. For the trajectories that started from b-TS2, if a trajectory ran from this transition state did not fully react to form products within 1 ps, the trajectory was allowed to run for an additional 1 ps. Velocities for each trajectory were reversed to also verify the backward path toward the reactants.

D. Analysis. Viewing of nuclear motion for all trajectories, along with creation of movie snapshots for the progression of the nuclei, were done with XMakeMol.\textsuperscript{60} The velocity autocorrelation functions for each of the C–O bonds in the two \( \text{CH}_3\equiv\text{O} \) fragments and the O–H bond in ‘OH fragment formed from \( \text{CH}_3\text{OCH}_2\text{OCH}_2\text{OOH} \) dissociation via p-TS2 were calculated for each of the 10 trajectories starting from p-TS2. The velocity autocorrelation functions for each of the C–O bonds in the two formaldehyde fragments and ‘OH O–H bond were averaged over the 10 trajectories. The Fourier transform of these three average velocity autocorrelation functions were performed using the XmGrace plotting package,\textsuperscript{61} yielding power spectra for each of the three bonds (C–O #1, C–O #2, and the O–H).

A “lifetime” curve was constructed by counting the number of HOOCH\(_2\text{OCHOH} \) that had not dissociated to HPMF (deuterated) and ‘OH by a given time. For dissociation of HOOCH\(_2\text{OCHOH} \) via b-TS1, HOOCH\(_2\text{OCHOH} \) was de-
Å, whereas the C- fragment 2, since its C- contrast, fragment 1 (see Figure 2) is derived from an sp^3 hybridized carbon atom. Upon formation, this fragment is

transition state, the C-

molecules and (b) the

function for (a) each of the C-

spectrum in part a is for the C-

-transition state is commonly utilized for probing formation of *OH, and the ro-vibrational state of *OH is an important consideration.

The power spectrum of the O–H stretch of the *OH radical product is shown in Figure 3b. Interestingly, a peak at 5231 cm\(^{-1}\) is close to the harmonic first overtone of the O–H (deuterium) stretch in *OH (deuterium) (5382 cm\(^{-1}\)). This is also red-shifted from the harmonic overtone peak, also due to anharmonicity. Thus, some of *OH radicals may have a vibrationally excited O–H stretch when produced from *CH\(_2\)-OCH\(_2\)OOH decomposition via p-TS2. This may have implications for quantitative measurement of *OH by laser-induced fluorescence (LIF).\(^{32}\) In LIF, the A ^2E \(\rightarrow \) X ^1H electronic transition is commonly utilized for probing formation of *OH, and the ro-vibrational state of *OH is an important consideration.\(^{62}\)

The total system energy is defined as \(E_{\text{total}} = E_{\text{ab}}(\text{CH}_2=\text{O#1}) + E_{\text{ab}}(\text{CH}_2=\text{O#2}) + E_{\text{int}}(\text{OH}) + E_{\text{trans}}(\text{CH}_2=\text{O#1}) + E_{\text{trans}}(\text{CH}_2=\text{O#2}) + E_{\text{rot}}(\text{OH})\). For each fragment is the sum of the fragments’ vibrational and rotational energies, and \(E_{\text{trans}}\) is the fragment’s translational energy. See the following footnotes for an explanation of how the vibrational, rotational, and translational energies were calculated.\(^3\) Estimated by subtracting out the linear and angular momentum contributions to the total internal plus translational energy.\(^4\) Estimated from the instantaneous rigid rotor approximation for each fragment (calculated from the angular momentum and its principal moments of inertia).\(^5\) Estimated from center of mass motion of each fragment with respect to the center of mass of the total system.

transition state, the C–O bonds in each fragment shorten. In contrast, fragment 1 (see Figure 2) is derived from an sp^3 hybridized carbon atom. Upon formation, this fragment is expected to have a lot of hydrogen wagging movement in and out of the plane and a little more C–O bond stretching than fragment 2, since its C–O bond shrinks from 1.323 to 1.207 Å, whereas the C–O bond of the terminal radical end CH\(_2\)=O moiety shrinks less, from 1.306 to 1.207 Å (according to DFT-B3LYP/6-31G** geometry optimization).

The power spectra of the average velocity autocorrelation function for the C–O bonds in the two formaldehyde molecules appear in Figure 3a. These two spectra show clusters of peaks around the fundamental frequency (1789 cm\(^{-1}\) according to DFT-B3LYP/6-31G**) and the first overtone (3578 cm\(^{-1}\) of the C–O stretch in both CH\(_2\)=O molecules formed from p-TS2. For CH\(_2\)=O #1 (see Figure 2), another cluster of peaks appears close to the second overtone (5367 cm\(^{-1}\)). The red shift of the C–O overtone stretches are likely due to the

**TABLE 1: Estimated Breakdown of the Internal and Translational Energy Content (in kcal/mol) for the Two Formaldehyde and *OH Fragments from *CH\(_2\)OCH\(_2\)OOH Dissociation (Averaged over 10 Trajectories)**

<table>
<thead>
<tr>
<th>energy type</th>
<th>CH(_2)=O #1 energy</th>
<th>CH(_2)=O #2 energy</th>
<th>*OH energy</th>
<th>total energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>vibrational</td>
<td>20 ± 5</td>
<td>13 ± 5</td>
<td>4 ± 3</td>
<td></td>
</tr>
<tr>
<td>rotational</td>
<td>3 ± 1</td>
<td>4 ± 2</td>
<td>1 ± 1</td>
<td></td>
</tr>
<tr>
<td>translational</td>
<td>10 ± 2</td>
<td>7 ± 2</td>
<td>4 ± 3</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>33 ± 5</td>
<td>24 ± 5</td>
<td>9 ± 3</td>
<td>66 ± 5</td>
</tr>
</tbody>
</table>

* The total system energy is defined as \(E_{\text{total}} = E_{\text{ab}}(\text{CH}_2=\text{O#1}) + E_{\text{ab}}(\text{CH}_2=\text{O#2}) + E_{\text{int}}(\text{OH}) + E_{\text{trans}}(\text{CH}_2=\text{O#1}) + E_{\text{trans}}(\text{CH}_2=\text{O#2}) + E_{\text{rot}}(\text{OH})\). For each fragment is the sum of the fragments’ vibrational and rotational energies, and \(E_{\text{trans}}\) is the fragment’s translational energy. See the following footnotes for an explanation of how the vibrational, rotational, and translational energies were calculated.\(^3\) Estimated by subtracting out the linear and angular momentum contributions to the total internal plus translational energy.\(^4\) Estimated from the instantaneous rigid rotor approximation for each fragment (calculated from the angular momentum and its principal moments of inertia).\(^5\) Estimated from center of mass motion of each fragment with respect to the center of mass of the total system.
B. Trajectories from b-TS1 on the Way to Hydroperoxymethyl Formate.

Chain-branching begins with the addition of O$_2$ to $\text{CH}_2\text{OCH}_2\text{OOH}$ to form $\text{O}_2\text{CH}_2\text{OCH}_2\text{OOH}$. $\text{OCH}_2\text{OOH}$ can dissociate back to $\text{CH}_2\text{OCH}_2\text{OOH}$ and O$_2$, or it can undergo hydrogen-transfer isomerization to form HOOCH$_2$OC$\equiv$HOOH:

\[
\text{HOOCH}_2\text{OC}\equiv\text{HOOH} \quad (1)
\]

The HOOCH$_2$OCHOH is expected to be a very short-lived, metastable species. It undergoes dissociation via scission of the O–O bond to produce HPMF and *OH.

\[
\text{HOOCH}_2\text{OC} \cdot \text{OH} \rightarrow \text{HOOCH}_2\text{OC}(=\text{O})\text{H} + \cdot\text{OH} \quad (2)
\]

Reactions 1 and 2 are depicted in Figure 5 as a potential energy surface (PES) profile, according to our previous DFT-B3LYP damped-dynamics simulations.\(^5\) Note that HPMF and *OH are expected to be formed with substantial excess energy because of the ~46 kcal/mol drop to the HPMF + *OH well from HOOCH$_2$OCHOH’s “plateau” on the PES.

1. Lifetime of HOOCH$_2$OCHOH. The lack of a true minimum energy well on the potential surface for HOOCH$_2$OCHOH suggests that it is a metastable intermediate of limited lifetime (see Figure 5). Thus, we set out to characterize exactly that. 70 trajectories were started from the deuterated b-TS1 transition state. In each case, we see a rapid migration of the transferring deuterium from the second carbon in OOC$\equiv$HOOH to the terminal oxygen (as expected from the PES generated with damped dynamics). Our dynamics show that the HOOCH$_2$OCHOH is formed ~8 fs into each trajectory. The lifetime of the HOOCH$_2$OCHOH should be accessible with short-time dynamics, since its lifetime calculated from conventional transition state theory (CTST) is 216 fs at 600 K.\(^{30}\) Our dynamics results more or less agree with this rough CTST estimate: HOOCH$_2$OCHOH dissociates within 500 fs of its formation. Two of these 70 trajectories exhibited recrossing of this deuterium back to the original carbon site to recreate OOC$\equiv$HOOH. Thus, there is a finite probability for recrossing the b-TS1 barrier. This is reasonable, since reaction 1 is endothermic by $\Delta H_0 = 14.9 \text{ kcal/mol}$, according to our previous DFT-B3LYP calculations\(^5\) ($\Delta E = 10.4 \text{ kcal/mol}$, according to Figure 5). Moreover, the nascent HOOCH$_2$OCHOH is only ~8 kcal/mol below the b-TS1 transition state. Of course, such recrossing will produce deviations in kinetics predicted by CTST, which assumes no recrossing of the products over the transition state barrier to re-form reactants.

At first glance, it may be reasoned that this recrossing could be due to excess energy in the reaction coordinate. However, comparing the initial energies along the reaction coordinate of the trajectories involving recrossing with those that did not recross, we see that the “nonrecrossing” trajectories have initial reaction coordinate kinetic energies that are distributed above and below those of the trajectories exhibiting recrossing. Thus, initial reaction coordinate energy is not a likely contributor to recrossing. Instead, a more likely origin of recrossing is the...
rotation about the O–O bond upon H-transfer in \(^{1}OOC\)H\(_{2}\)O\(_{2}\) to form HOO\(_{2}\)CH\(_{2}\)OHOH. If rotation around this bond is not rapid or sufficient enough, recrossing is most likely. Since the thermal selection of velocities favors excitation of low frequency modes, corresponding to the internal torsional motion, over high frequency bending and stretching modes, recrossing would be more prevalent at relatively low temperatures and less prevalent with increasing temperature. Thus, chain-branching reactions starting through reaction 1 could be inhibited initially because of some reversal of reaction 1 at relatively low temperatures (below 600 K). However, recrossing is slight at 600 K. As might be expected, coupling between the reaction coordinate and the stretching and bending degrees of freedom may be important in the recrossing process, but the torsional motion along the backbone destroys the favorable conformation for recrossing. Further work is needed to examine dynamics at temperatures above and below 600 K to validate the recrossing phenomenon.

With the remaining 68 successful trajectories (i.e., trajectories that involved dissociation of HOO\(_{2}\)CH\(_{2}\)OHOH into HPMF and \(^{1}O\)H), the lifetime for HOO\(_{2}\)CH\(_{2}\)OHOH in each trajectory was used to generate a plot of the number of undissociated radicals vs time (in femtosecond). An exponential form was expected, where \(N(t) \approx N_0 \exp(-\tau t)\). Here \(N(t)\) is the number of undissociated HOO\(_{2}\)CH\(_{2}\)OHOH radicals at a given time \(t\), \(N_0\) is the initial number of HOO\(_{2}\)CH\(_{2}\)OHOH radicals, and \(\tau\) is the lifetime (inverse of the rate).\(^{63}\) Though many more trajectories than our humble 68 would be needed for an excellent statistical sampling, the plot of the number of dissociated HOO\(_{2}\)CH\(_{2}\)OHOH radicals vs time shown in Figure 6 has unexpected non-RRKM (i.e., nonergodic) behavior. Rather than following the expected ergodic exponential curve, the lifetime curve most closely fits a half-Gaussian shape (with a correlation of 0.996). Microcanonical selection of the initial conditions was also tried to see if the Gaussian shape was an artifact of the canonical selection of initial conditions. Almost identical qualitative results were obtained with microcanonical initial conditions. RRKM theory is a microcanonical theory. However, convolution of microcanonical RRKM with a Boltzmann factor gives a canonical result, which will also be exponential in character if the unimolecular dynamics is ergodic.

RRKM theory\(^{57,64,65}\) assumes that the internal energy distribution is random and complete, and the random lifetime distribution is expected to be of an exponential form \(P(t) = k \exp(-kt)\) where \(k\) is the rate of decay of an activated complex and \(t\) is the time.\(^{66}\) The time for energy transfer is assumed to be negligible compared to \(1/k.\)\(^{56}\) The overall behavior illustrated in Figure 6 may appear to be Gaussian, but this curve can be viewed in three parts. The first part, the top of the “Gaussian” (0–88 fs), shows slow dissociation of the HOO\(_{2}\)OHOH radical, where only 28% have dissociated.

This observation of nonexponential behavior is indicative of “apparent” non-RRKM behavior due to chemical activation.\(^{57,66}\) Slow IVR seen here can be likened to Rabinovitch and co-workers’ classic example of apparent non-RRKM behavior: chemical activation to prepare vibrationally excited hexafluorobicyclpropyl-\(d_2\), with subsequent decomposition via elimination of CF\(_{3}\), where elimination of CF\(_{3}\) is not immediate because chemical activation occurs on the opposite side of the molecule to where CF\(_{3}\) is eliminated.\(^{68}\) Upon formation, HOO\(_{2}\)CH\(_{2}\)OHOH has energy localized on the H-transfer side of the radical (the left side according to the chemical formula). Excess kinetic energy from \(^{1}OOC\)H\(_{2}\)OCH\(_{2}\)OH isomerization is expected to be pocketed in the newly formed H–O bond. This energy would take some nonnegligible amount of time to transfer along the H–O–C–O–C–O–C–O–H backbone from the side with the newly formed H–O bond to the opposite side of the radical to hasten O–O scission. This could be why we see a nonexponential decrease in the number of nondissociated HOO\(_{2}\)CH\(_{2}\)OHOH with time. It is apparent from Figure 6 that the newly formed HOO\(_{2}\)CH\(_{2}\)OHOH does not dissociate immediately for the majority of trajectories. There appear to be a few trajectories with sufficient energy for O–O rupture in the first 88 fs of HOO\(_{2}\)CH\(_{2}\)OHOH formation. However, there is a dramatic decrease in the number of HOO\(_{2}\)CH\(_{2}\)OHOH radicals between 88 and 167 fs when a majority (41%) of the HOO\(_{2}\)CH\(_{2}\)OHOH is depleted. This second dissociation segment will be discussed next.

Another possible contribution to the nonergodic behavior seen in Figure 6 is the potential need for a proper HOO\(_{2}\)CH\(_{2}\)OHOH conformation that allows for O–O scission. Thus, the second segment, exhibiting a precipitous drop in surviving HOO\(_{2}\)CH\(_{2}\)OHOH radicals vs time near 167 fs shown in Figure 6 has unexpected non-RRKM (i.e., nonergodic) behavior. Rather than following the expected ergodic exponential curve, the lifetime curve most closely fits a half-Gaussian shape (with a correlation of 0.996). Microcanonical selection of the initial conditions was also tried to see if the Gaussian shape was an artifact of the canonical selection of initial conditions. Almost identical qualitative results were obtained with microcanonical initial conditions. RRKM theory is a microcanonical theory. However, convolution of microcanonical RRKM with a Boltzmann factor gives a canonical result, which will also be exponential in character if the unimolecular dynamics is ergodic.

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We observe in the molecular dynamics that the “ring” in b-TS1 must open up. That is, the first five heavy atoms of the HO–O–C–O–C–O–OH backbone must rotate with respect to each other until the newly formed “HO” end is sufficiently far away from the C radical center. Though this is not the only factor in HOO\(_{2}\)CH\(_{2}\)OHOH dissociation (the HOO\(_{2}\)CH\(_{2}\)OHOH that dissociate within the first 88 fs seem to have quite a bit of vibrational energy in the O–O bond or in deuterium wag of the adjacent radical carbon, which also disrupts the \(\pi\) network), “unraveling” of the first five heavy centers of the b-TS1 ring seems to be a factor in the HOO\(_{2}\)CH\(_{2}\)OHOH lifetimes greater than 100 fs. Mode-specificity effects involving initial coupling to the reaction
coordinate have led to biexponential behavior of the survival probability in the direct-dynamics simulations of Doubleday et al.\textsuperscript{37,38} We may suspect the same of this second segment, but with a limited amount of data in this segment, we can only fit a single exponential (see Figure 6).

The final segment beyond 167 fs may involve trajectories (31\%) where the HOOCH\textsubscript{2}OCHOH has lost memory of the initial configuration, and therefore may be more ergodic in dissociation. This final depletion of HOOCH\textsubscript{2}OCHOH, gradually dropping off after 167 fs, has been fit to an exponential curve (see Figure 6).

**2. Energy distributions of HPMF and ‘OH.** Following the dissociation of HOOCH\textsubscript{2}OCHOH, its dissociation products “fall” into a deep potential chasm. After crossing b-TS\textsubscript{1}, the products can gain a maximum of about 54 kcal/mol of excess internal (vibrational and rotational) and translational energy (on top of (hydrogenated) zero-point energy of 50 kcal/mol and thermal energy of \~22 kcal/mol). However, the damped dynamics trajectory used to generate the PES in Figure 5 leads to a loosely bound HOOCH\textsubscript{2}OC(=O)H vs ‘OH complex. About 5 kcal/mol is required to separate HOOCH\textsubscript{2}OC(=O)H vs ‘OH. Thus, the maximum energy gain is actually \~49 kcal/mol. With such an energy gain, it may be possible that HPMF gains a substantial amount of internal energy to react immediately via the many decomposition paths available to it (see Figure 1).

Upon decomposition, however, the ‘OH radical leaves with a fraction of this energy. An estimated breakdown of the vibrational, rotational, and translation energies imparted to both HPMF and ‘OH is listed in Table 2. HPMF apparently is formed with an estimated 61 kcal/mol internal and translational energy (including zero point and thermal energy). Most of this internal energy is vibrational energy (\~87\%). There is some rotational energy (\~8\%) and recoil translational energy (\~5\%). Though rotational energy may aid in dissociation of HPMF, it is not as effective as internal vibrational energy for unimolecular decomposition of molecular systems.\textsuperscript{37,64} The estimated vibrational energy of 53 kcal/mol in HPMF is only about 17 kcal/mol above the zero-point energy of deuterated HPMF (36.2 kcal/mol). The lowest barrier to HPMF unimolecular dissociation is through the formation of a hydrogen-bonded HC(=O)OH vs CH\textsubscript{2}OO complex, which is about 32 kcal/mol above the energy for HPMF (30 kcal/mol when zero-point energy is considered); another 12 kcal/mol is needed to fully dissociate the loose HOOH, its dissociation products HOOH, and the translational energy of HOOH translational energy distribution of Figure 8. The possible trimodality seen in Figure 8 may be related to the reaction coordinate to HOOCH\textsubscript{2}OC(=O)OH translational energy component of Figure 8. Not the possible trimodal character of the distribution.

HC(=O)OH vs CH\textsubscript{2}OO complex to HC(=O)OH and CH\textsubscript{2}OO. Only 13\% of the HPMF molecules formed in our simulations have sufficient internal energy (above the zero-point energy) to surmount this barrier. The mean internal energy (above the zero-point energy) of the HPMF is 22 kcal/mol with a standard deviation of 7 kcal/mol (see Figure 7 to view the distribution of energies). Thus, most HPMF may not have enough energy to undergo unimolecular dissociation upon formation and may require activation via collisions to decompose. Unfortunately, the number of degrees of freedom for HPMF along with the inclusion of a model to simulate collisions (either implicitly or explicitly) makes direct DFT-B3LYP BOMD of the HPMF decomposition process computationally prohibitive.

‘OH contains an estimated 31\% of the internal and translational energies of the HPMF and ‘OH. Unlike HPMF, most of this energy is in translational motion (about 64\%). This translational energy accounts for about 20\% of the total energy (see Table 2). The distribution of ‘OH translational energy appears in Figure 8. There is a small negative correlation between the lifetime of HOOCH\textsubscript{2}OCHOH and the translational energy of ‘OH (correlation coefficient of \~0.3), which is expected since translational motion of ‘OH occurs along the reaction coordinate to HOOCH\textsubscript{2}OCHOH dissociation. Thus, the possible trimodality seen in Figure 8 may be related to the three-stage behavior seen in the lifetime curve in Figure 6. The early time decay into HPMF + ‘OH may be associated with the fast (high kinetic energy) ‘OH component of Figure 8.

### Table 2: Estimated Breakdown of the Internal and Translational Energy Content (in kcal/mol) for the HPMF and ‘OH Fragments from HOOCH\textsubscript{2}OCHOH Dissociation (Averaged over 68 Trajectories)

<table>
<thead>
<tr>
<th>energy type</th>
<th>HPMF energy</th>
<th>‘OH energy</th>
<th>total energy</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>vibrational\textsuperscript{b}</td>
<td>53 ± 7</td>
<td>7 ± 4</td>
<td>60 ± 7</td>
<td>\footnote{The total system energy is defined as }</td>
</tr>
<tr>
<td>rotational\textsuperscript{c}</td>
<td>5 ± 3</td>
<td>3 ± 2</td>
<td>8 ± 5</td>
<td></td>
</tr>
<tr>
<td>translational\textsuperscript{d}</td>
<td>3 ± 1</td>
<td>18 ± 3</td>
<td>21 ± 4</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>61 ± 7</td>
<td>28 ± 4</td>
<td>89 ± 7</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Estimated by subtracting out the linear and angular momentum contributions to the total internal plus translational energy.

\textsuperscript{b} Estimated from center of mass motion of each fragment with respect to the center of mass of the total system.

\textsuperscript{c} Estimated from instantaneous rigid rotor approximation for each fragment (calculated from the angular momentum and its principal moments of inertia).

\textsuperscript{d} Estimated by subtracting out the linear and angular momentum of deuterated HPMF (36.2 kcal/mol).
However, the origin of the later time decay components of Figure 6 is unclear. The bending and stretching motions of the HOOCH2OC reaction system, resulting in a more ergodic distribution of those HOOCH2OCHOOH that decay at later times.

About 25% of the energy imparted to \(^{1} \text{OH}\) is vibrational (Table 2). The \(~7\) kcal/mol of vibrational energy is \(~3\) kcal/mol higher than zero-point energy. However, not all trajectories conserve zero-point energy (35% had vibrational energies below 3.8 kcal/mol). The zero-point leakage problem is a well-known problem with the classical propagation of the nuclei, and techniques have been proposed to treat this problem.71,72,73,74 Using the Einstein–Keller–Brillouin (EKB) binning,54 we find that about 47% of the \(^{1} \text{OH}\) can be assigned to the \(v = 1\) state, while one out of the 68 trajectories has an \(^{1} \text{OH}\) in \(v = 2\). Thus, 49% (almost half) of the \(^{1} \text{OH}\) created from HOOCH2OCHOOH is vibrationally excited, which is an important consideration for quantitative determination of \(^{1} \text{OH}\) from LIF probing of the \(\Sigma^{+} \rightarrow \Sigma^{-} \Pi\) electronic transition.62 Again, these likely correspond to the slower moving \(^{1} \text{OH}\) radicals formed.

C. HPMF Decomposition. According to our conventional transition state theory results, the HPMF decomposition path with the lowest barrier to reaction (HPMF to CH2OO\dot{}\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
OH). The kinetics of HPMF decomposition via b-TS2 is only slightly more favorable than the HPMF decomposition via b-TS5.

Ten trajectories from b-TS5 and ten trajectories from b-TS5′ were run in the forward direction toward the HPMF decomposition products CH2OO + HC(=O)OH and CH2OȮ + HC(=O)-OH, respectively. These trajectories only yielded CH2OO and slightly more favorable than the HPMF decomposition via 1402

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The snapshots of a representative trajectory showing the rearrangement of the initial HC(=O)OH + HCO + OH products to form H2O + HC(=O)OC(=O)OH (formic acid anhydride). The dark gray balls are oxygens, the light gray balls are carbons, and the white balls are deuteriums. The brown balls are HC(=O)OH and CH2OȮ. The initial products are HC(=O)OH + HCO + OH. At 230 fs, the OH fragment reacts with the nascent HC(=O)OH. At 300 fs, H2O approaches the formoxyl radical, and at 350 fs we see that the H2O and formoxyl radical have formed formic acid anhydride (FAA, HC(=O)OC(=O)H).

When re-formation of HPMF does not occur, the formic acid and HCOOH metastable radical do not readily separate. Then, 10 of the 30 trajectories yield fully formed HCO, *OH, and HC(=O)OH.

However, another 10 of the 30 trajectories unexpectedly show the HC(=O)OH⋯HCOOH complex rearranging to form formic acid anhydride (HC(=O)OC(=O)H; FAA) and H2O:

\[ \text{HC(=O)OH⋯HCOOH} \rightarrow \text{HCO} + \text{OH} + \text{HC(=O)OH} \]

(4)

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\[ \text{HC(=O)OH⋯HCOOH} \rightarrow \text{HC(=O)OC(=O)H} + \text{H}_2\text{O} \]

(5)

Snapshots of a representative trajectory showing the rearrangement of HCOOH to H2O + FAA are shown in Figure 10. The snapshot at 230 fs shows that the nascent *OH formed from the short-lived HCOOH complex is close enough to attack the deuterium of the nascent formic acid molecule to form H2O. This water molecule is formed vibrationally excited (there is little to no barrier for this deuterium abstraction). This is not the first time that the high reactivity of *OH has been demonstrated in molecular dynamics simulations. Frank et al.79 have shown in their DFT-B3LYP MD simulations of *OH reacting with 3-hexanone that the *OH, having a highly electrophilic character, readily forms H-bonded complexes and van der Waals adducts, which eventually can lead to formation of highly vibrationally excited H2O.

The remaining formoxyl and HCO fragments are in close enough proximity to combine to form FAA (see 300 fs snapshot of Figure 10). This is a fairly long-ranged attraction since both formoxyl and HCO are radical species. Thus, their recombination is barrierless and the resulting FAA is highly vibrationally excited (as with the H2O). The drive to form H2O and FAA can also be partly but not entirely (since the system is not at equilibrium) explained with thermodynamics. Figure 11 shows a detailed illustration of the paths leading to HPMF decomposition including an HPMF decomposition path leading to H2O and FAA. The path leading to H2O + FAA has a barrier higher than those of the paths considered in Figure 1. Thus, it was not considered to be a viable path for HPMF decomposition. However, compared with the products from paths with lower barriers, the H2O and FAA products are much more thermodynamically favorable than the other HPMF decomposition products from more kinetically favorable paths. Unlike other pathways, the decomposition of HPMF to H2O + formic acid anhydride is an exothermic reaction: −52.7 kcal/mol at the DFT-B3LYP/6-31G** level of theory.28,35 We see from our molecular dynamics that the simple picture of direct formation of FAA being disfavored kinetically is not relevant once dynamics is taken into account; subsequent rearrangements after going through the kinetically favored paths allow its formation to occur. FAA and H2O are known to be common decomposition products of HPMF under atmospheric conditions.26 Under diesel engine conditions, however, we expect numerous collisions to occur with the molecules present in the engine. Unfortunately, we cannot easily incorporate collisions of the possible molecules that HPMF could encounter because of the computational expense. It is expected that HPMF’s highly reactive radical products would easily react with many of the combustion species they collide with (including dimethyl ether itself), thereby somewhat limiting production of FAA.

Rather than producing FAA after *OH removes the hydroxyl deuterium from the nascent HC(=O)OH to form H2O and formoxyl radical (as in Figure 10), the HCO radical also lose its deuterium to the formoxyl radical to produce CO and a new HC(=O)OH:

\[ \text{HC(=O)OH⋯HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} + \text{HC(=O)OH} \]

(6)

This occurs in two of the 30 trajectories. Snapshots of one of the trajectories are shown in Figure 12. At 165 fs, the nascent *OH radical abstracts the hydroxyl deuterium from the HC(=O)OH fragment. In the snapshot at 280 fs, the deuterium of the nascent HCO is transferred to the formoxyl radical. The oxygen of the newly formed H2O is close to this deuterium and appears to be aiding the deuterium transfer process. H2O, CO, and
HC(=O)OH are much more stable products than *OH, HCO, and HC(=O)OH: $\Delta H_f(298 \text{ K}) = -174.7 \text{ kcal/mol}$ for the former group of hydrogenated species and $\Delta H_f(298 \text{ K}) = -70.8 \text{ kcal/mol}$ for the latter group of hydrogenated species. One trajectory leads to the creation of two rather than one HC(=O)OH:

$$\text{HC(=O)OH} \cdots \text{HC(O)OH} \rightleftharpoons \text{HC(=O)OH} + \text{HC(=O)OH}\tag{7}$$

Selected snapshots for this trajectory are shown in Figure 13. The trajectory starts off on the same course as the trajectories leading to FAA + H₂O and H₂O + CO + HC(=O)OH, with the nascent *OH heading toward abstraction of the hydroxyl deuterium of the newly formed formic acid molecule. However, the HCO is in close proximity to the *OH radical as it makes its way toward the hydroxyl deuterium. When *OH attacks this hydroxyl deuterium, the radical carbon of HCO latches on to the *OH and forms a new HC(=O)OH (see the snapshot at 630 fs in Figure 13). In this trajectory, it seems that HC(=O)OH aids in rearranging HC(OH) to produce a second formic acid. As with the previous two cases described above, the formation of two HC(=O)OH is more thermodynamically probable ($-181.0 \text{ kcal/mol}$) than the formation of *OH, HCO, and HC(=O)OH ($-70.8 \text{ kcal/mol}$).

The rearrangement of *OH, HCO, and HC(=O)OH to form FAA and H₂O was not the only unexpected outcome seen in our 30 trajectories from b-TS2. One of the 30 trajectories underwent rearrangement of the HC(OH) and HC(=O)OH fragments to form the Criegee intermediate CH₂OO and HC(=O)OH:

$$\text{HC(=O)OH} \cdots \text{HC(O)OH} \rightleftharpoons \text{CH₂OO} + \text{HC(=O)OH}\tag{8}$$

Snapshots from a representative trajectory showing the rearrangement of HCOOH and HC(=O)OH to form CH₂OO and HC(=O)OH are shown in Figure 14. In this case, the HCOOH does not fully dissociate to form HCO and *OH as seen in the previous case of FAA + H₂O production (Figure 10). Instead, a “lining-up” of both the radical orbital of HCOOH with the hydroxyl deuterium of HC(=O)OH and of the hydroxyl deuterium of the HCOOH with the carbonyl oxygen of the HC(=O)OH occurs in the first few hundred femtoseconds. A failed attempt of transferring the HC(=O)OH hydroxyl deuterium occurs at 320 fs. A second attempt at this deuterium transfer occurs around 500–515 fs, which is successful. The transfer of the hydroxyl deuterium of the HC(=O)OH to HC(OH) at 515 fs is promptly followed by a transfer of the hydroxyl deuterium of HCOOH to the carbonyl oxygen of HC(=O)OH at 530 fs. By 600 fs, there are discernible CH₂OO and HC(=O)OH fragments. The lowest lying path of HPMF dissociation involves the formation of CH₂OO⋯HC(=O)OH through b-TS5’ (see Figure 11). This path involves a transfer of the peroxide hydrogen on HPMF to the carbonyl oxygen on the other side of the HPMF molecule along with a C–O stretch, as depicted in Figure 9. This path leads to a product, CH₂OO⋯HC(=O)OH, that is lower in energy than the *OH, HCO, and HC(=O)OH produced through b-TS2. Thus, the formation of CH₂OO⋯HC(=O)OH, like FAA + H₂O, is both a thermodynamically and kinetically favorable outcome.

To further explore the kinetics and thermodynamics of the products observed in these simulations starting from b-TS2, we have listed the $\Delta G$, $K_{eq}$, branching ratios calculated from $K_{eq}$ and from the MD trajectories for all reactions starting from b-TS2 in Table 3. From the equilibrium constants and their respective branching ratios, it can be argued that the most likely reaction to take place is reaction 6, closely followed by reaction
branching ratios from the dynamics show that reaction 4 and reaction 5 have the most dominant products from b-TS2. The products of reaction 4 are thus clearly kinetically controlled products, but the products of reaction 5 appear equally likely, suggesting that their favorable thermochemistry plays an important role in their appearance. Reactions 5–7 are the most thermodynamically favorable. However, these products are the result of multiple steps after b-TS2, and, therefore, are likely to not be kinetically favorable. This could explain the relatively low branching ratios of the products of reactions 6 and 7.

So, 30 trajectories is too limited of a sampling for gathering statistics on the myriad of products that may be observed in our trajectories from b-TS2. Though the path through b-TS2 is not the most favorable path to HPMF decomposition (see Figure 11), the trajectories ran from b-TS2 do show us that the many paths to decomposition of this highly oxygenated compound are interconnected. Since all paths to HPMF decomposition are interconnected from a dynamics point-of-view, this is bound to have an effect on the underlying kinetics, namely that the low-temperature chain branching kinetics of DME is more complex than once thought.3,33,30

IV. Summary and Conclusions

We present Born–Oppenheimer molecular dynamics (BOMD) simulations for selected portions of the deuterated DME chain propagation and chain branching potential energy surfaces. Although our notation throughout refers to “H” rather than “D” for simplicity, the dynamics were all performed on deuterated species to justify the classical treatment of nuclei in the BOMD method. Thus, our calculations will underestimate the reaction dynamics/kinetics whenever tunneling may be important. Nevertheless, our short-time dynamics reveal complex, intriguing behavior not predicted by conventional statistical rate theories (e.g., CTST and RRKM). We studied three areas of the chain propagation and branching PESs where short-time dynamics had the prospect of showing interesting phenomena. The first of these regions was along the chain propagation pathway for DME oxidation, involving the dissociation of \( \text{CH}_2\text{OOH} \) to form two \( \text{CH}_2\text{==O} \) and \( \cdot \text{OH} \). Trajectories were started at p-TS2 (the transition state for dissociation of \( \cdot \text{CH}_2\text{OCH}_2\text{OOH} \) in the
TABLE 3: The Free Energy Change, the Equilibrium Constant, and the Number of Trajectories Representing the Outcome of Each Respective Competing b-TS2 Reaction (at the DFT-B3LYP/6-31G** Level of Theory with Deuterated Species)\textsuperscript{a}

<table>
<thead>
<tr>
<th>reaction</th>
<th>corresponding equation\textsuperscript{b}</th>
<th>$\Delta G$ (kcal/mol)</th>
<th>$K_{eq}$ from $K_{eq}$ simulations</th>
<th>branching ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMF $\rightarrow$ HCO + OH + HCl($\rightarrow$O)OH</td>
<td>4</td>
<td>$-4.5$</td>
<td>$4.42 \times 10^4$</td>
<td>$1.1 \times 10^{-33}$</td>
</tr>
<tr>
<td>HPMF $\rightarrow$ HC($\rightarrow$O)OC($\rightarrow$O)H + H$_2$O</td>
<td>5</td>
<td>$-75.9$</td>
<td>$4.51 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>HPMF $\rightarrow$ CO + H$_2$O + HCl($\rightarrow$O)OH</td>
<td>6</td>
<td>$-94.9$</td>
<td>$3.63 \times 10^{-4}$</td>
<td>0.89</td>
</tr>
<tr>
<td>HPMF $\rightarrow$ HC($\rightarrow$O)OH + HCl($\rightarrow$O)OH</td>
<td>7</td>
<td>$-92.4$</td>
<td>$4.62 \times 10^{-8}$</td>
<td>0.11</td>
</tr>
<tr>
<td>HPMF $\rightarrow$ CH$_2$OO + HCl($\rightarrow$O)OH</td>
<td>8</td>
<td>20.3</td>
<td>$4.04 \times 10^{-8}$</td>
<td>$9.9 \times 10^{-43}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The temperature and pressure for these calculations were 600 K and 1 atm, respectively. \textsuperscript{b} As enumerated in the text.

Forward direction toward the products, two CH$_2$=O and *OH. Maricq et al.\textsuperscript{32} reported that the rate of CH$_2$=O formation in their real-time laser photolysis experiments was slow compared to the rate derived by Sehested et al.\textsuperscript{31} using indirect smog chamber techniques. They attributed this slow rate of CH$_2$=O formation to excited C=O stretching in the nascent CH$_2$=O, which would be invisible to the diode laser probing the $\nu = 0 \rightarrow 1$ C=O stretch transition. The power spectra of the average C=O and O-H velocity correlation functions constructed by us shows that the C=O stretch of formaldehyde exhibits first and second (clustered) overtone peaks, which lends credence to Maricq et al.'s\textsuperscript{32} proposal that the excited C=O formaldehyde stretch is the source of apparent slow formaldehyde appearance. Moreover, the C=O stretch appears to be strongly coupled to the other bending and stretching vibrational modes, which involve C-H bonds. This may be a possible reason for the initial invisibility of the formaldehyde to the diode laser probe in the experiments of Maricq et al. The *OH radical may be formed vibrationally excited as well.

Simulations started in the forward direction from b-TS1, the isomerization transition state from *OCH$_2$OCH$_2$OOH to HOOCH$_2$OCHOOH along the DME chain-branching path, show that a small number of trajectories (2 out of 70, or 3%) recross the b-TS1 barrier. This recrossing is to be expected, since the formation of the short-lived metastable radical HOOCH$_2$OCHOOH from *OCH$_2$OCH$_2$OH is very endothermic and the barrier to recrossing b-TS1 to re-form *OCH$_2$OCH$_2$OH is only $\sim 8$ kcal/mol (see Figure 5). This shows that HPMF + *OH formation along the chain branching path may be inhibited by recrossing to re-form *OCH$_2$OCH$_2$OOH. Since low-frequency torsional modes important along the reaction path are weighted more in the thermal momentum and coordinate displacement selection than high-frequency bending and stretching modes, we would expect to see an increase in recrossing at temperatures lower than 600 K, because the torsion of the nascent OH group seems to be the dominant factor in inhibiting recrossing to re-form *OCH$_2$OCH$_2$OOH.

For the remaining 68 trajectories where recrossing does not occur, the lifetime of HOOCH$_2$OCHOOH does not demonstrate an ergodic (RRKM) pattern of dissociation to HPMF and *OH. The survival probability instead follows a Gaussian-like falloff. However, the behavior of the HOOCH$_2$OCHOOH lifetime can be understood by dividing the plot into three regions. The first region (0–88 fs) may be indicative of "apparent" non-RRKM behavior via chemical activation. Upon formation of HOOCH$_2$OCHOOH via b-TS1, the nascent H–O in which most of the newly gained 8 kcal/mol is expected to be located is on the opposite side of the radical from where O–O dissociation will occur. Therefore, it is expected that this energy is slow to dissipate throughout the radical to allow for ergodic dissociation of HOOCH$_2$OCHOOH to HPMF and *OH. However, an "intrinsic" non-RRKM process may also occur, which could explain the sharp decline in surviving HOOCH$_2$OCHOOH molecules in the 88–167 fs region. The right orientation may need to be achieved by torsional motion of the H–O–O–C=O–C–O–O–H backbone to allow for dissociation of the short-lived HOOCH$_2$OCHOOH complex. More ergodic behavior is observed after 167 fs as the internal energy becomes more randomly distributed in the remaining HOOCH$_2$OCHOOH radicals.

An estimate of the internal and translational energies of the important chain-branching intermediate HPMF shows that while most of the internal and translational energy is in the vibrational modes of the HPMF (\textasciitilde 59%), this energy is on average only about 17 kcal/mol above zero-point energy for HPMF and may be insufficient for unimolecular decomposition of HPMF, which requires surmounting barriers of at least 42 kcal/mol. Interestingly, the *OH has \textasciitilde 20% of the estimated internal and translational energy in translation (the second highest energy partition after the vibrational energy of HPMF). Since the breaking of the O–O bond involves the translation of the *OH, it is not surprising that the *OH translational energies are somewhat correlated with the lifetime of HOOCH$_2$OCHOOH, exhibiting a possible trimodal distribution as in the characteristic decay times shown in Figure 6. We caution that the 70 trajectories from b-TS1 do not represent an exhaustive sampling of the phase space for this system, and further trajectories are required to confirm the observations made here.

Last, we investigated the unimolecular decomposition of HPMF starting from the b-TS2, b-TS5, and b-TSS’ transition states (see Figure 11). The latter two types of trajectories did not yield any unusual dynamics over 1 ps, but the former trajectories through b-TS2 did yield unexpected short-time dynamics. The decomposition of HPMF through b-TS2 to form HC($\rightarrow$O)OH + HCO + *OH is endothermic (\textasciitilde 39 kcal/mol), and the reverse reaction to re-form HPMF has a barrier of only \textasciitilde 7 kcal/mol. In the 30 trajectories started from b-TS2, a loose complex of HC($\rightarrow$O)OH and HCOOH is formed, which in six trajectories (20%) recross b-TS2 to re-form HPMF. In 10 trajectories (33%), the HC($\rightarrow$O)OH, HCO, and *OH fully separate. Because of unfavorable thermodynamics (see Table 3), one must consider these products as kinetically controlled. However, in the remaining 14 trajectories (47%), the loose complex of HC($\rightarrow$O)OH and HCOOH rearranges to form products that are more thermodynamically favorable than HC($\rightarrow$O)OH + HCO + *OH. These products include formic acid anhydride (FAA; HC($\rightarrow$O)OC($\rightarrow$O)H) + H$_2$O, HC($\rightarrow$O)OH + CO + H$_2$O, HC($\rightarrow$O)OH + HC($\rightarrow$O)OH, and CH$_2$OO + HC($\rightarrow$O)OH. All of these stable products except for CH$_2$OO have been observed in (hydrogenated) DME combustion experiments.\textsuperscript{33,35} Arrangements of unstable products from HPMF decomposition may need to be taken into account for more quantitative kinetics modeling of the stable product ratios presented in the experimental work of Curran et al.\textsuperscript{33} and Liu et al.\textsuperscript{35} Though many more trajectories would be needed to establish definitive branching ratios for these products (and
reveal any other possible rearrangements of HC(=O)OH and HCOOHO), these results are suggestive that the unimolecular decomposition HPMF does not exclusively form unstable radical species such as *OH, *OCH(=O)H, HCO, and CH₂OO that are ready for further bimolecular reactions. These radicals can be attracted by other fragments in the HPMF unimolecular decomposition process and produce thermodynamically stable species, thereby potentially stifling further oxidation of the DME fuel. This is not a prediction that could have been made with simple statistical rate theories.

The inhibition of further reaction of the DME chain branching intermediate HPMF by both the recrossing of b-TS1 from HOOCH₂OCHOH to *OCH₂OCH₂OH via hydrogen transfer and by the rearrangement of HCO + *OH + HC(=O)OH to form thermodynamically more stable products represent dynamic mechanisms that may limit production of *OH. With a diminished supply of *OH (i.e., less than two *OH per consumed DME molecule), first-stage DME autoignition due to chain branching is expected to be somewhat hindered.

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**Supporting Information Available:** A table of DFT-B3LYP/6-31G** frequencies and zero-point vibrational energy for the deuterated species considered in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


(23) Andersen and Carter


(78) ΔH(298 K) for formyl (HCO2) calculated from the ΔHf(298 K) of HCO2 dissociating to CO2 and H derived from DFT-B3LYP/6-311G* total energies, zero-point vibrational energies (ZPVE) and C_p(298 K)’s for HCO2, H, and CO2 (−6.5 kcal/mol) calculated by us and known experimental ΔHf(298 K)’s for H (52.1 kcal/mol) and CO2 (−94.1 kcal/mol) from the NIST Standard Reference Database 69, March 2003 Release; NIST Chemistry WebBook.