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Theoretical Study of the Mechanisms and Kinetics of the Reactions of Hydroperoxy (HO₂) with Hydroxymethylperoxy (HOCH₂O₂) and Methoxymethylperoxy (CH₃OCH₂O₂)

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ABSTRACT

The reactions of hydroperoxy with hydroxymethylperoxy and methoxymethylperoxy have been studied using the hybrid density functional theory and the coupled-cluster theory with the complete basis set extrapolation. In contrast to the unsubstituted alkylperoxy reactions, it is revealed that the OH-substitution has significant effect on the reaction mechanism. Several hydrogen-bonding reaction precursors exist at the entrance. The reaction pathways show strongly anisotropic character. The transition states prefer to be four-, five, six-, or seven-membered cyclic structures. The predicted coefficients rate are expressed as $k(T) = 8.48 \times 10^{-24} T^{3.55} e^{2164/T} + 2.37 \times 10^{-29} T^{4.70} e^{3954/T} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. In comparison with the available experimental data in the temperature range 275 - 333 K, the agreement between theory and experiment is fairly reasonable with the relative average deviation of only 8%. It is shown that the nascent products are hydroperoxide molecules and hydroxyl radicals at low and high temperatures, respectively. Meanwhile, the potential source for the production of formic acid has been found and new insights on the experimental observation are presented.

I. Introduction

Organic peroxy radicals (RO₂) are of central importance in the global and regional atmospheric chemistry.¹⁻⁵ The reactions of RO₂ with nitric oxide play a crucial role for tropospheric ozone formation in the polluted environment. The reactions of RO₂ with hydroperoxy (HO₂) have been recognized as sinks for peroxy radicals and as terminators for ozone-generation chain reactions.^{2,3} The mechanisms and kinetic data of these reactions are highly desired in order to build the atmospheric models and to develop the structure-activity relationships.

The HO₂+RO₂ reactions have attracted considerable interests experimentally and theoretically.⁶⁻²¹ However, due to the inherent difficulties in the studies of the radical-radical reactions, neither mechanistic nor kinetic data have been well established for the HO₂+RO₂ reactions up to date especially for the substituted RO₂ species. For instance, the reactions of alkylperoxy radicals with HO₂ take place via the following mechanisms:⁵

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$
(1a)
$$\rightarrow RO + OH + O_2$$
(1b)
$$\rightarrow ROH + O_3$$
(1c)

For the simple alkylperoxy radicals, e.g., $C_2H_5O_2$ radical, the predominant product channel has been determined to be (1a).^{12,13} However, it was suggested that the product channels (1b) and (1c) are of significance as well for the reactions of HO₂ with the substituted alkylperoxy radicals such as the oxygenated peroxy radicals.^{14,15} Recently, Jenkin and coworkers investigated the products of the HO₂ + CH₃OCH₂O₂ reaction using the long-path FTIR spectroscopy.¹⁶ The OH radical was

determined to be one of the reaction products. Its yield was estimated indirectly to be 19%, although the detailed reaction mechanisms were still unknown. Therefore, seeking a fundamental understanding of the HO_2+RO_2 reactions through the systematical theoretical investigations might provide some new insights for the complementary experiments.

Two experimental studies of the HO₂ + HOCH₂O₂ reaction are available.^{17,18} The rate coefficients have been measured at 275 – 333 K by Veyret and co-workers using flash photolysis kinetic spectroscopy.¹⁷ It was found that the reaction takes place relatively faster than the other reactions between HO₂ and alkylperoxy radicals. For instance, the room-temperature rate coefficient is approximately 1.2×10^{-11} cm³molecule⁻¹s⁻¹, which is twice of that for the HO₂ + CH₃O₂ reaction. The overall rate coefficients show negative temperature dependence. The measured apparent activation energy is –4.6 kcal/mol, which is the lowest yet reported among the HO₂ + RO₂ reactions. The reaction mechanism was studied by the same authors using the technique of modulated photolysis–long path kinetic spectroscopy at 2 Torr and 298 K.¹⁸ The Cl₂-CH₂O-O₂ mixture was photolyzed to make the condition [HO₂] >> [HOCH₂O₂] in order to minimize the influence of the side reactions. Two major product channels were determined:

$$HO_2 + HOCH_2O_2 \rightarrow HOCH_2OOH + O_2$$
(2a)
$$\rightarrow HCOOH + ?$$
(2b)

It was concluded that the yield of formic acid (HCOOH) is approximately 40%. The co-product of HCOOH was not determined experimentally. Note that in these static experimental studies, the nascent product molecules or radicals cannot be detected directly. Therefore, the yields of the products were obtained using the simulation of a complex reaction mechanism, rather than a direct

measurement. Moreover, the secondary or chain reactions cannot be excluded from the system and thus the estimated reaction mechanism might be questionable with significant uncertainty. Meanwhile, although the experimental low-temperature kinetics are of atmospheric concern, the $HO_2 + RO_2$ reactions could play an importance role in the oxidation combustions of various organic fuels. Mechanistic and kinetic simulations at high temperatures for the $HO_2 + RO_2$ reaction are highly desired as well for combustion models.

Although the RO₂ reactions have attracted considerable interests both experimentally and theoretically, a general understanding of their contributions to the atmospheric and combustion processes is scarce. We have carried out the systematical computational studies on the reactions of HO₂ with CH₃O₂, C₂H₅O₂, CH₂FO₂, and CH_{3-x}Cl_xO₂ radicals.^{12,20,21} In order to build *a priori* quantitative structural-activity relationship for the HO₂+RO₂ reactions by search through all possible hydroperoxy radical reactions of atmospheric importance, the reactions of HO₂ with two oxygenated peroxy radicals, namely, HOCH₂O₂ and its methyl substitute CH₃OCH₂O₂, have been characterized theoretically in this work. The detailed reaction mechanisms for both reactions are revealed for the first time. The rate coefficients are calculated in a wide range of temperatures (200 – 2000 K) using the variational transition state theory.²²

II. Computational Details

The geometries of reactants, intermediates (IM), transition states (TS), and products were fully optimized using the hybrid density functional theory B3LYP²³ with the triple-zeta 6-311G(d,p)

basis set. Harmonic vibrational frequencies were calculated at the same level of theory for the characterization of stationary points (minimum or transition state) and for the zero-point energy (ZPE) corrections. The Gibbs free energy (G) was calculated using the statistical thermodynamics with the rigid rotor harmonic oscillator (RRHO) approximation to the contributions of translation, rotation, and vibration.²⁴ All transition state involved in the title reaction were explored using Berny algorithm developed by Schlegel.²⁵ The intrinsic reaction coordinate (IRC)^{26,27} calculations were carried out to verify the predicted transition states connecting the designated reactants and products.

On the basis of the B3LYP/6-311G(d,p) optimized geometries, two higher-level *ab initio* methods were employed to calculate the single-point energies. The first method is the composite model CBS-QB3 developed by Petersson and co-workers.²⁸ The second method is the coupled-cluster theory with single, double, and non-iterative triple excitations [CCSD(T)]²⁹ with Dunning's correlation- consistent double- and triple-zeta basis sets (cc-pVDZ and cc-pVTZ).³⁰ Moreover, the complete basis set (CBS) limit was estimated using the following formula:^{31,32}

$$E_{HF}^{X} = E_{HF}^{\infty} + ae^{-bX}, \qquad \Delta E_{corr}^{X} = \Delta E_{corr}^{\infty} + \frac{c}{X^{3}},$$

where E_{HF}^{∞} and ΔE_{corr}^{∞} are the HF energy and the correlation energy at the CBS limit. X = 2, 3, 4are the cardinal numbers for the cc-pVXZ basis sets. The five parameters, namely, E_{HF}^{∞} , ΔE_{corr}^{∞} , a, b, c are determined uniquely using three HF energies E_{HF}^{X} (HF/cc-pVDZ, HF/cc-pVTZ, and HF/cc-pVQZ) and two CCSD(T) correlation energies ΔE_{corr}^{X} [CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ]. The total CCSD(T)/CBS energy is the sum of E_{HF}^{∞} and ΔE_{corr}^{∞} . For the sake of comparing with the previous work¹², the results of CCSD(T)/CBS//B3LYP/6-311G(d,p) method are used to discuss the title reaction in the following sections. Due to the large size of the HO₂ + CH₃OCH₂O₂ reaction, only the CCSD(T)/cc-pVDZ method was employed to calculate the single-point energies on the basis of the B3LYP/6-311G(d,p) optimized geometries. The good performance of the CCSD(T)/cc-pVDZ//B3LYP/6-311G(d,p) level of theory has been demonstrated previously.¹² All the *ab initio* calculations were carried out using the Gaussian03 programs in the current work.³³

III. Results and Discussion

ROCH₂O₂(R=H, CH₃) and HO₂ are reactive radicals containing the unpaired electrons with a spin of s=1/2, and thus both species are in their doublet ground states since the spin multiplicity is 2s+1=2. Therefore, two doublets combine into the total spin of either |1/2+1/2| = 1 or |1/2-1/2| = 0. For the sake of the spin conservation, the association of HO₂ and ROCH₂O₂ could undergo on the singlet and triplet potential energy surfaces, respectively. The mechanisms for the HO-substituted alklyperoxy reactions are more complicated than the non-substituted alkylperoxy reactions investigated previously.^{12,20,21} On the triplet surface, the reaction proceeds via the hydrogen abstraction, the concerted elimination, and the S_N2-type displacement. On the singlet surface, the direct hydrogen abstraction and the addition/elimination mechanisms are revealed. Both surfaces will be discussed in details. The relative energies for various product channels involved in the HO₂ + HOCH₂O₂ reaction calculated at the CCSD(T)/CBS//B3LYP/6-311G(d,p) level of theory are in excellent agreement with the experimental values (Table S1). The averaged absolute deviation is only 1.47 kcal/mol.

1. Mechanisms of the HO₂ + HOCH₂O₂ Reaction

A. Triplet Reactions. Direct H-abstraction reaction is the most important mechanism on the triplet surface. Since there are three types of hydrogen atoms for the reactants (Figure S1), the H-abstraction reaction between HO₂ and HOCH₂O₂ can take place via six pathways, as exhibited in Figure 1. The corresponding geometries and energies of the intermediates (IM) and transition states (TS) are shown in Figure 2 and Table 1, respectively. Three pathways via TS-T1, TS-T2, and TS-T3 correspond to the hydrogen abstraction from HO_2 by $HOCH_2O_2$, forming the ground-state oxygen and HOCH₂OOH. Evidently, these reaction routes involve either negative or very minor net barriers with respect to the initial reactants and all are highly exothermic. The barrier for TS-T1 appears to be the lowest, which is only 0.95 kcal/mol above the reactants in terms of ΔG In view of the geometrical parameters, all three TS correspond to the reactant-like barriers. The breaking HO bond is elongated by at most 10% and the forming OH bond is at least 30% longer than the equilibrium value. Interestingly, the order for the breaking OH bonds is TS-T1 < TS-T2 < TS-T3but that for the forming OH bonds is in reverse. The rest of pathways are the hydrogen abstraction from HOCH₂O₂ by HO₂, forming H₂O₂ with significant barriers. Therefore, the hydromethyl hydroperoxide rather than hydroperoxide should be one of the major products.

In contrast to the alkylperoxy reactions, a distinguished feature of the $HO_2 + HOCH_2O_2$ reaction is that the H-abstractions involve various hydrogen-bonding complexes at the entrance. As shown in Figure 2, the hydrogen bonding for the precursors IM-T1 and IM-T2 occurs between the hydrogen atom of HO_2 and the terminal O atom of $HOCH_2O_2$. IM-T3 is the most stable complex with the binding free energy of 5.12 kcal/mol. It involves an eight-member-ring geometry with double hydrogen bonds which are slightly shorter than those of IM-T1 and IM-T2. The IM-T6 complex is a floppy seven-membered cyclic structure involving two hydrogen bonds. Unlike IM-T3, one of the hydrogen bonds of IM-T6 occurs between the hydrogen atom of HO₂ and the lone-pair electron orbital of the mediate oxygen atom of HOCH₂O₂. The only pathway involving IM-T6 is its concerted decomposition to form CH₂O and two HO₂ radicals via a significant barrier TS-T8. In fact, this mechanism can be considered as the HO₂-mediated decomposition of the HOCH₂O₂ radical.

B. Singlet Reactions. The predominant mechanism for the HO₂ + HOCH₂O₂ reaction on the singlet surface is addition/elimination. The OO association between the two terminal O atoms of HO₂ and HOCH₂O₂ leads to the tetroxide compound HOCH₂O₄H. Analogous to the other HO₂ + RO₂ reactions reported, ^{12,20,21} there is no barrier along the addition path. The association process is exothermic by around 8 kcal/mol in terms of ΔG . A total of eight conformations of HOCH₂O₄H were found (Figure S2) together with the respective internal rotation barriers (Table S2) in view of three dihedral angles (HOOO, OOOO, and OOOC). The most stable conformation is denoted as IM-S1 in Figure 3, which is due to the hydrogen-bonding interaction between the two terminal OH groups. Because the inter-conversion barriers between the conformers are below the initial reactants, it is conceivable that the addition products should be a mixture of all eights conformers. Due to the flexible O₄ geometry of IM-S1, many decomposition reactions can take place subsequently as illustrated in Figures 3 and 4. The corresponding energetic data of IM and TS are summarized in Table 2.

Formic acid (HCOOH) could be formed via four pathways. TS-S1 involves a four-membered cyclic structure. The OO bond and one of the CH bonds are breaking simultaneously to form HO₃H and HCOOH. Although this channel is highly exothermic, the barrier for TS-S1 is as high as 27 kcal/mol in terms of ΔG . TS-S2 has a five-membered cyclic structure with a nearly in-the-plane geometry. One of the H atoms is shifted to the O atom and the OO bond is breaking. Simultaneously, the terminal OH group is leaving away to form the free radical. The barrier height is ~20 kcal/mol and the route is exothermic significantly. It is worth noting that TS-S2 can be viewed as a transition state for the HO₂-mediated unimolecular decomposition of HOCH₂O₂. The barrier for the HOCH₂O₂ \rightarrow HCOOH+OH reaction is nearly twice of that for TS-S2. The six-membered transition state to form HCOOH was denoted as TS-S3 in Figure 3. The two OO bonds in TS-S3 are breaking simultaneously to form the singlet O_2 molecule. Meanwhile, one of the CH bonds is breaking and the H atom is approaching to the terminal OH group to form H₂O molecule. This channel is the most exothermic path among the mechanisms considered in this work. However, the barrier for TS-S3 was calculated to be 35.23 kcal/mol in terms of ΔG , which prevents this channel from occurring at room temperature. The previous assumption¹⁸ that the formic acid were produced via the six-membered intermediates might be excluded theoretically. The last HCOOH production mechanism involves TS-S4 with a seven-membered cyclic structure. The hydrogen atom of the CH bond is forming H_2 molecule with the terminal H atom, and simultaneously the breaking OO bond leads to the ozone molecule. Although this channel is still exothermic, the barrier for TS-S4 is more than 48 kcal/mol, and thus this channel could be excluded as well. Therefore, all four reaction routes leading to formic acid involve cyclic transition states. The lowest barrier is the five-membered TS-S2 rather than the six- or seven-membered

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cyclic structures. In comparison with the hydrogen abstraction mechanisms on the triplet surface where no or little net barrier exists, the direct formation of HCOOH on the singlet surface might not be plausible at least at low temperatures (e.g., below 300 K).

Interestingly, the inclusion of cyclic transition state appears to be a general feature for the decomposition mechanisms of the tetroxide adduct. The formation of O_2 +HOCH₂OOH occurs via the four-membered TS-S5. Rather than a concerted bond breaking process, the HO bond in TS-S5 has been almost broken but the OO bond is only stretched slightly. The five-membered transition state TS-S6 leads to dihydroxyl methane and ozone. The terminal H atom is shifting to the O atom and the ozone molecule is forming by breaking the OO bond. The breaking OH bond is stretched by about 20% while the OO bond is almost broken completely. Two seven-membered transition states were found for the formation of water. For TS-S7, water molecule is formed between the OH group of the HOCH₂O₂ moiety and the H atom of the HO₂ moiety. For TS-S8, water molecule is formed between the OH group of the HO₂ moiety and the H atom of the HOCH₂O₂ group.

Two simple bond cleavage reactions of HOCH₂O₄H, namely, forming HO + HOCH₂O₃ and HO₃ + HOCH₂O, respectively, have been considered. Both pathways are barrierless as proved by the scan calculations and are endothermic by about 7~8 kcal/mol. Apparently, the HOCH₂O–O₃H bond is fairly weak. Moreover, neither HOCH₂O₃ nor HO₃ is stable with respect to the subsequent OO bond-fission products, leading to the final products HOCH₂O + OH + O₂ which is exothermic by ~16 kcal/mol. Therefore, the formation of HOCH₂O and OH radicals might be feasible.

The direct hydrogen abstraction pathways on the singlet surface were investigated for completeness. Depending on the relative orientations of HO₂ toward HOCH₂O₂, two transition states, namely, TS-S9 and TS-S10, were found (Figure 3). Both transition states are early barriers since the OH bond is only slightly stretched and the forming OH bond is far away from the equilibrium distance. The barrier heights for TS-S9 and TS-S10 are relatively high due to the possible repulsion interactions between the oxygen atoms of the O₄ ring structure. The last pathway examined on the singlet surface is the production of CH₂O and two HO₂ radicals via TS-S11. Analogous to TS-T8, it represents another HO₂-mediated mechanism for the unimolecular decomposition of HOCH₂O₂. In fact, the structures and energies of TS-S11 are essentially the same as those of TS-T8.

2. Kinetic Analysis

To deduce the relative importance of various product channels in the $HO_2 + HOCH_2O_2$ reaction, the rate coefficients have been calculated using transition state theory as a function of temperatures (200 – 2000 K) at pressure of 2 Torr helium bath gas in accordance with the low-pressure experiments. For the triplet reactions, only three direct channels producing O_2 and HOCH₂OOH were considered:

 $HO_{2} + HOCH_{2}O_{2} \leftrightarrow IM-T1^{*} \rightarrow TS-T1 \rightarrow {}^{3}O_{2} + HOCH_{2}OOH$ $↔ IM-T2^{*} \rightarrow TS-T2 \rightarrow {}^{3}O_{2} + HOCH_{2}OOH$ $↔ IM-T3^{*} \rightarrow TS-T3 \rightarrow {}^{3}O_{2} + HOCH_{2}OOH$

where "*" indicates the internally excited species. On the singlet surface, the simplified reaction

mechanism was employed, viz .:

$$\begin{split} \mathrm{HO}_2 + \mathrm{HOCH}_2\mathrm{O}_2 &\leftrightarrow \mathrm{IM}\text{-}\mathrm{S1}^* \to \mathrm{TS}\text{-}\mathrm{S1} \to \mathrm{HCOOH} + \mathrm{HO}_3\mathrm{H} \\ &\to \mathrm{TS}\text{-}\mathrm{S2} \to \mathrm{HCOOH} + \mathrm{OH} + \mathrm{HO}_2 \\ &\to \mathrm{TS}\text{-}\mathrm{S6} \to \mathrm{CH}_2(\mathrm{OH})_2 + \mathrm{O}_3 \\ &\to \mathrm{TS}\text{-}\mathrm{S7} \to \mathrm{CH}_2\mathrm{O} + \mathrm{H}_2\mathrm{O} + \mathrm{O}_3 \\ &\to \mathrm{HOCH}_2\mathrm{O} + \mathrm{HO}_3 \to \mathrm{HOCH}_2\mathrm{O} + \mathrm{OH} + \mathrm{O}_2 \\ &\to \mathrm{HOCH}_2\mathrm{O}_3 + \mathrm{OH} \to \mathrm{HOCH}_2\mathrm{O} + \mathrm{OH} + \mathrm{O}_2 \\ &\to \mathrm{HOCH}_2\mathrm{O}_3 + \mathrm{OH} \to \mathrm{HOCH}_2\mathrm{O} + \mathrm{OH} + \mathrm{O}_2 \end{split}$$

The deactivation rate of the IM-S1 adduct was estimated using the exponential-down energy transfer mode.³⁴ The energy transfer parameters, $-\langle \Delta E \rangle_{\text{down}} = 100 \text{ cm}^{-1}$, and the Lennard-Jones (12-6) collisional efficiency parameters, $\varepsilon = 100 \text{ K}$, $\sigma = 5.0 \text{ Å}$, were employed in the calculation. Since the contribution from the stabilization of IM-S1 to the overall reaction rate is of significance only at very low temperatures and high pressures, the rate coefficient is insensitive to the above empirical parameters at the low pressure of our interest. For the tight transition states (e.g., TS-S1, S2, S6, and S7), the RRHO approximation was used to evaluate sum and densities of states at the energy/angular momentum (E/J) resolved level. Quantum tunneling was included using the Eckart formula.35 For the barrierless pathways, namely, the association of HO2 with HOCH2O2, the decomposition of IM-S1 to produce $HOCH_2O + HO_3$ and $HOCH_2O_3 + OH$, the interaction potentials between the two fragments were built by summing the bonding potentials for the reacting OO bonds and the pairwise LJ(12-6) nonbonding potentials for the rest of inter-fragment atoms. The OO bonding interaction was calculated using the Morse potential, i.e., $V_M = D_e \left[1 - e^{-\beta(R-R_e)} \right]^2 - D_e$, where the binding energy D_e and the equilibrium bond distance

 R_e were taken directly from the *ab initio* data. The range parameter β was estimated using the formula, $\beta = 2\pi c \tilde{v} \sqrt{\frac{\mu}{2D_e}}$, where the vibrational frequency, \tilde{v} , and the reduced mass μ were obtained at the B3LYP/6-311G(d,p) level of theory. The β parameters for the HOCH₂O₂–O₂H, HOCH₂O–O₃H, and HOCH₂O₃–OH bonding interactions are 4.62, 5.34, and 3.43 Å⁻¹, respectively. The empirical LJ(12-6) potential parameters for H, C, and O atoms were taken directly from the literature.³⁶ The evaluation of the number and density of states were carried out variationally using the flexible transition state theory as implemented in the Variflex program.³⁷

Note that the transition probability between the singlet and triplet surfaces was not treated explicitly in the present calculations. The singlet-triplet transition probability has been assumed to be marginal because of the forbidden spins. Our extensive attempts to calculate the single-triple conical interaction for the entrance of the HO₂+HOCH₂O₂ association have not been successful due to the convergence difficulties of the multireference configuration interactions. The complete active spaces (CAS) calculations with all valence electrons are unaffordable at present. Therefore, more rigorous treatment of the singlet-triplet transition has to be reserved for further study.

The rate coefficients were calculated using the CCSD(T)/CBS energies and the B3LYP/6-311G(d,p) optimized geometrical parameters and frequencies. The results are shown in Figure 5 in comparison with the experimental data. The theoretical rate coefficients are significantly lower than the experimental data. In order to obtain the apparent agreement between theory and experiment, the barrier heights for the triplet reactions have to be lowered systematically by roughly 1 kcal/mol. Such an adjustment is reasonable in view of the uncertainty

of the *ab initio* energetic data, namely, ± 2 kcal/mol of chemical accuracy. Interestingly, if the CCSD(T)/cc-pVDZ calculated energies were employed, the rate coefficients are in good agreement with the experimental data with the relative error of only 8%. Moreover, the experimentally observed negative temperature-dependence of the rate coefficients can be well reproduced theoretically at low temperatures. In fact, the barrier heights obtained at the CCSD(T)/cc-pVDZ level for the triplet abstraction paths are generally lower by 1 kcal/mol than those at the CCSD(T)/CBS level (Table 1). Certainly the better performance of the CCSD(T) calculation with a smaller basis set should be just a coincidence.

The rate coefficients for the singlet reactions increase monotonically with the temperature. However, the rate coefficients for the triplet reactions show negative temperature dependence below 600 K and change to be positive at higher temperatures. For practice, the overall rate coefficients were fitted to the following empirical expression,

$$k(T) = 8.48 \times 10^{-24} T^{3.55} e^{2164/T} + 2.37 \times 10^{-29} T^{4.70} e^{3954/T}$$

for T = 200 - 2000 K in the unit of cm³molecule⁻¹s⁻¹.

At lower temperatures (e.g., T < 400 K), the HO₂ + HOCH₂O₂ reaction is dominated by the triplet H-abstraction mechanism. The major direct products should be the ground state O₂ and HOCH₂OOH. The branching ratio for the singlet channels is less than 10% (Figure 5). As the temperature increases, the singlet paths become more and more significant. At 1000 K, the singlet and triplet mechanisms have almost equal contributions to the overall reaction. Therefore, the high-temperature production of the OH radical in the HO₂+HOCH₂O₂ reaction could be predicted

on the basis of the current theoretical simulations.

Experimentally, it was deduced that HCOOH is the direct product of the HO₂ + HOCH₂O₂ reaction with a yield of about 40% at room temperature.^{17,18} However, the present theoretical calculation shows that O₂ and HOCH₂OOH are the only direct products. Since all the possible mechanisms for the formation of formic acid have been considered in this work, the alternative mechanism for the HCOOH production has to be investigated. It is worth noting that the experimentally observed HCOOH was determined by fitting a complex reaction mechanism, where many secondary reactions might occur in the mixture. Therefore, a few additional sources besides the HO₂ + HOCH₂OOH reaction, the O₂ + HOCH₂OOH reaction, and the unimolecular decomposition of HOCH₂OOH since the concentration of HO₂ is much higher than that of HOCH₂O₂ in the experiments.^{17,18} Unlike the regular thermalized HOCH₂OOH molecule, the nascent HOCH₂OOH product in the title reaction is energy rich due to the significant exothermicity. Four energetically stable HOCH₂OOH conformations (Figure S3) could be populated statistically with a large amount of available energies.

Eight hydrogen abstraction pathways for the $HO_2 + HOCH_2OOH$ reaction have been studied (Figure 6). Four C-H^{...}O₂H abstraction routes lead to $HCOOH+OH+H_2O_2$ and the other four O-H^{...}O₂H abstractions produce the Criegee radicals $HOCH_2OO$ (Figure S4). The corresponding barrier heights are only one-third of the maximum available energy to $HOCH_2OOH$. Furthermore, the formation of HCOOH is more exothermic than that of Criegee radicals. Therefore, the reaction of HOCH₂OOH with HO₂ might be a potential source for formic acid with the co-products hydroxyl radicals and hydroperoxide.

For the O_2 + HOCH₂OOH reaction, three C-H⁻⁻O₂H abstraction pathways leading to HCOOH have been found (Figure S4 and S5). As could be seen from the significant barriers, the reactivity of O_2 molecule toward HOCH₂OOH is much weaker than that of the HO₂ radical. Meanwhile, the unimolecular decomposition of HOCH₂OOH undergoes via the simple bond-fission processes or the four-center elimination transition state (Figure S6). Apparently, the barriers involved in these reaction routes are generally higher than the maximum available energy to HOCH₂OOH. Therefore, HCOOH can only be produced effectively in the secondary reaction of HO₂ with HOCH₂OOH. Under the typical experimental condition,¹⁸ the HO₂ + HOCH₂OOH reaction can be competitive with the HO₂ + HOCH₂O₂ reaction. In the consideration of the experimental yield of HCOOH, it is estimated that nearly half of the HOCH₂OOH molecules would react further with HO₂ radicals and the other half is deactivated collisionally to the final stable product.

3. The HO₂ + CH₃OCH₂O₂ Reaction

Energetic pathways of the $HO_2 + CH_3OCH_2O_2$ reaction are very similar to those of the HO_2 + $HOCH_2O_2$ reaction, as shown in Figure 7. Moreover, the optimized geometries of the stationary points involved in these two reactions are also nearly the same except for the CH_3O - and HOgroups (Figure S7). Therefore, the methyl substitution has only marginal effect on the mechanisms for the HO_2 +ROCH₂O₂ reaction. On the triplet surface, the direct hydrogen abstractions produce CH₃OCH₂OOH and ground-state O₂ molecules via hydrogen-bonding precursors. On the singlet surface, the tetroxide CH₃OCH₂O₄H adduct is formed via the barrierless OO association. The hydrogen bonding occurring between the terminal OH group and the OCH_3 group can gain extra stabilization energy for the tetroxide. Analogous to the $HO_2 + HOCH_2O_2$ reaction, the transition states for the decomposition of CH₃OCH₂O₄H involve the N-membered cyclic geometries as well (Figure S7). The four- and six-membered cyclic transition states, as suggested previously by Wallington et al.,¹⁹ have been optimized successfully at the B3LYP/6-311G(d,p) level of theory in this work (e.g., TS-S1 and TS-S2 in Figure S7). The corresponding products are CH₃OCH₂OOH and CH₃OCHO, respectively. However, the barriers for these two transition states are too high to be important in the reaction although the $CH_3OCHO + H_2O + O_2$ channel is the most exothermic path. The energetically most favorable reaction routes include the CH₃OCHO+HO₂+OH channel via TS-S4 and the direct OO bond cleavage channel to form $CH_3OCH_2O + HO_3$ or $CH_3OCH_2O +$ HO + O2. The five-membered cyclic TS-S4 represents the transition state for the HO2-mediated unimolecular decomposition of $CH_3OCH_2O_2$. In addition, there are two direct hydrogen abstraction channels on the singlet surface. In contrast to the energetically favorable triplet abstraction pathways, the singlet abstractions involve significant barriers.

It is worth noting that that $Gro\beta$ et al. reported an experimental study on the reaction of HO₂ with $CH_3C(O)O_2$ using a combination of laser-induced fluorescence and transient absorption spectroscopy.³⁹ As demonstrated by the previous theoretical calculations on this reaction,^{40,41} the $CH_3C(O)O_2$ radical behaves very differently from the alkyl-substituted $CH_3OCH_2O_2$ radical because the former is a carbonyl-substituted RO_2 . Our extensive *ab initio* mechanistic and kinetic

simulations on the HO_2 + $CH_3C(O)O_2$ reaction will be reported elsewhere.

IV. Concluding Remarks

The reaction mechanism of the HO₂ + HOCH₂O₂ reaction has been predicted using the CCSD(T)/CBS//B3LYP/6-311G(d,p) and CBS-QB3 methods. The reaction takes place either on triplet potential energy surface via the hydrogen abstraction routes to form hydroxymethyl hydroperoxide and oxygen molecules or on singlet potential energy surface via the addition-elimination mechanism to form various radical products. It is revealed that the triplet pathways play dominant role at low temperatures and the addition-elimination mechanism for formic acid, the secondary reaction of the HO₂ radical with the energy-rich HOCH₂OOH molecule has been proposed to account for the experimentally observed yields of HCOOH. The HO₂ + CH₃OCH₂O₂ reaction is very similar to the HO₂ + HOCH₂O₂ reaction in view of the energetic reaction pathways and the structures of the stationary points, indicating that the methyl substitution has only marginal effect on the reaction mechanism.

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Supporting Information

Zero-point energies (ZPE), relative energies (ΔE), and Gibbs free energies (ΔG) at 298.15 K for various products involved in the HO₂ + HOCH₂O₂, CH₃OCH₂O₂ reactions are listed in Tables S1-S3. The B3LYP/6-311G(d,p) optimized geometrical coordinates for all the species involved in this work are listed in Tables S4-S5. Geometries of the reactants, conformations, and the species involved in the secondary reactions are shown in Figures S1-S6. Geometries of intermediates and transition states involved in the HO₂ + CH₃OCH₂O₂ reaction are illustrated in Figure S7.

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Species	ZPE	$^{b}\Delta E_{1}$	$^{b}\Delta G_{1}$	$^{b}\Delta E_{2}$	$^{b}\Delta G_{2}$	$^{b}\Delta E_{3}$	$^{b}\Delta G_{3}$	$^{b}\Delta E_{4}$	$^{b}\Delta G_{4}$
IM-T1	40.92	-6.24	-3.39	-5.55	-2.70	-4.18	-1.33	-4.02	-1.17
TS-T1	39.8	-6.95	-3.20	-3.93	-0.18	-2.80	0.95	-2.26	1.49
IM-T2	40.63	-5.24	-4.22	-4.67	-3.65	-3.90	-2.88	-4.06	-3.04
TS-T2	38.57	-6.29	-3.68	0.51	3.12	0.96	3.57	-1.58	1.03
IM-T3	41.49	-11.63	-7.77	-11.11	-7.25	-8.98	-5.12	-7.97	-4.11
TS-T3	38.05	-9.92	-5.76	-2.54	1.62	-1.27	2.89	-1.52	2.64
TS-T4	37.28	13.92	18.65	17.51	22.24	17.94	22.67	16.09	20.82
TS-T5	36.64	16.21	19.25	21.59	24.63	20.3	23.34	18.73	21.77
IM-T4	40.08	8.72	11.73	8.37	11.38	8.09	11.1	8.54	11.55
IM-T5	40.71	-4.90	-2.53	-4.87	-2.50	-3.41	-1.04	-3.71	-1.34
TS-T6	37.35	3.76	11.21	18.35	25.8	19.22	26.67	19.57	27.02
TS-T7	38.86	18.47	20.96	31.75	34.24	31.82	34.31	30.88	33.37
IM-T6	41.17	-8.22	-4.71	-7.98	-4.47	-6.03	-2.52	-5.89	-2.38
TS-T8	36.01	8.55	13.03	14.49	18.97	17.34	21.82	18.15	22.63

TABLE 1. Zero-point energies (ZPE), relative energies (ΔE), and free energy (ΔG) at 298.15 K for various species on the triplet potential energy surface with respect to the HO₂ + HOCH₂O₂ asymptote.^{*a*}

^{*a*} Zero-point energy of the HO₂ + HOCH₂O₂ reactants is 39.37 kcal/mol. The total energies of the reactants are -416.466770, -415.956552, and -415.8501793 Hartrees at the B3LYP/6-311G(d,p), CCSD(T)/CBS, and CBS-QB3 levels of theory, respectively.

^b Subscripts 1, 2, 3, and 4 represent B3LYP/6-311G(d,p), CCSD(T)/cc-pVDZ, CCSD(T)/CBS, and CBS-QB3 levels of theory, respectively. All energies are in kcal/mol.

Species	ZPE	$^{b}\Delta E_{1}$	$^{b}\Delta G_{1}$	$^{b}\Delta E_{2}$	$^{b}\Delta G_{2}$	$^{b}\Delta E_{3}$	$^{b}\Delta G_{3}$
IM-S1	42.24	-9.18	-3.31	-15.13	-9.26	-14.22	-8.35
TS-S1	38.16	17.27	22.05	12.81	17.59	12.33	17.11
TS-S2	38.31	9.23	15.26	5.14	11.17	4.01	10.04
TS-S3	37.30	35.86	41.51	20.32	25.97	17.78	23.43
TS-S4	35.00	35.57	41.36	33.16	38.95	33.88	39.67
TS-S5 ^a	41.19	n/a	/	37.56	/	36.27	/
TS-S6	38.65	16.62	22.49	9.78	15.65	8.62	14.49
TS-S7	38.32	13.32	19.50	13.27	19.45	11.32	17.50
TS-S8	37.73	19.40	25.31	20.58	26.49	18.86	24.77
TS-S9	39.96	12.00	17.94	5.80	11.74	6.40	12.34
TS-S10	40.15	26.17	30.49	11.54	15.86	11.84	16.16
IM-S2	41.17	-8.21	-4.06	-6.01	-1.86	-3.43	0.72
TS-S11	35.98	8.55	17.03	17.39	25.87	21.83	30.31

TABLE 2. Zero-point energies (ZPE), relative energies (ΔE), and Gibbs free energies (ΔG) at 298.15 K for various species on the singlet potential energy surface with respect to the HO₂ + HOCH₂O₂ asymptote.

^a Geometry and ZPE were calculated at the CISD/cc-pVDZ level because of the failure of B3LYP optimizations.

^b Subscripts 1, 2, and 3 represent B3LYP/6-311G(d,p), CCSD(T)/CBS, and CBS-QB3 levels of theory, respectively. All energies are in kcal/mol.

Figure Captions

Figure 1. Schematic profiles for the triplet potential energy surface of the $HO_2 + HOCH_2O_2$ reaction. The relative free energies (ΔG , in kcal/mol) at 298.15 K are calculated at the CCSD(T)/CBS//B3LYP/6-311G(d,p) level.

Figure 2. The B3LYP/6-311G(d,p) optimized geometries of the intermediates (IM) and transition states (TS) on the triplet potential energy surface for the HO₂+HOCH₂O₂ reaction. Bond distances are in Å and bond angles are in degrees.

Figure 3. The B3LYP/6-311G(d,p) optimized geometries of the intermediates (IM) and transition states (TS) on the singlet potential energy surface for the HO₂+HOCH₂O₂ reaction. Bond distances are in Å and bond angles are in degrees.

Figure 4. Schematic profiles for the singlet potential energy surface of the HO₂ + HOCH₂O₂ reaction. The relative free energies (ΔG , in kcal/mol) at 298.15 K are calculated at the CCSD(T)/CBS//B3LYP/6-311G(d,p) level.

Figure 5. Theoretical rate coefficients for the $HO_2 + HOCH_2O_2$ reaction. Triangles with error bars are the experimental data in ref 1. Dashed line: the rate coefficients for the hydrogen abstractions on the triplet surface using the CCSD(T)/CBS // B3LYP/6-311G(d,p) *ab initio* data. Dotted line: the rate coefficients for

the reactions on the singlet surface using the CCSD(T)/CBS // B3LYP/6-311G(d,p) *ab initio* data. Dotted-dashed line: the rate coefficients for the hydrogen abstractions on the triplet surface using the CCSD(T)/cc-pVDZ // B3LYP/6-311G(d,p) *ab initio* data. Solid line: the overall rate coefficients. The branching ratios for the singlet reactions are shown by the line with solid circles.

Figure 6. Schematic profiles for the potential energy surface of the $HO_2 + HOCH_2OOH$ reaction. The relative free energies (ΔG , in kcal/mol) at 298.15 K are calculated at the CCSD(T)/CBS//B3LYP/6-311G(d,p) level.

Figure 7. Schematic profiles for the potential energy surface of the HO₂ + CH₃OCH₂OOH reaction. The relative free energies (ΔG , in kcal/mol) at 298.15 K are calculated at the CCSD/cc-pVDZ//B3LYP/6-311G(d,p) level.

Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7.



Graphical Abstract



The peroxy-peroxy radical reactions exhibit spin, conformation, and temperature dependence, forming formic acid and hydroxyl radicals.