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Dear reviewer,

Revision for Manuscript acp-2021-890

We thank you very much for giving us the opportunity to revise our manuscript. We highly appreciate the reviewer for their comments and suggestions on the manuscript entitled "**OH-initiated atmospheric degradation of hydroxyalkyl hydroperoxides: mechanism, kinetics, and structure-activity relationship**". We have made revisions of our manuscript carefully according to the comments and suggestions of reviewer. The revised contents are marked in blue color. The response letter to reviewer is attached at the end of this cover letter.

We hope that the revised manuscript can meet the requirement of Atmospheric Chemistry & Physics. Any further modifications or revisions, please do not hesitate to contact us.

Look forward to hearing from you as soon as possible.

Best regards,

Yu Huang

Comments of reviewer #1

1. The investigated HHPs are generated from the reactions of CH_2OO, anti-CH_3CHOO and $(CH_3)_2COO$ with water vapor, not considering the HHP from the bimolecular reaction of syn-CH_3CHOO with water. This should be stated.

   Response: Based on the Reviewer's suggestion, OH-initiated oxidation of hydroxyalkyl hydroperoxide (HHP), generated from the bimolecular reaction of *syn*-CH_3CHOO with water, has been added in the revised manuscript. The corresponding free-energy and electronic-energy potential energy surface (PES) are displayed in Figures S4 and S5, respectively. As shown in Figure S4, the H-abstraction by OH radical from $HOCH(CH_3)OOH$ has six kinds of pathways. For each pathway, a per-reactive complex is formed prior to the corresponding transition state, and then it overcomes modest barrier to reaction. The $\Delta G_a^{\#}$ of R6' and R8' are 2.3 and 1.8 kcal mol^{-1}, respectively, which are ~ 5 kcal mol^{-1} lower than those of R5' and R7'. This result shows that H-abstraction from the -CH (R6') and -OOH (R8') groups are preferable kinetically. Same conclusion is also derived from the energy barriers $\Delta E_a^{\#}$ that R6' and R8' the most favourable H-abstraction pathways (Figure S5). It should be noted that although the barriers of R6' and R8' are comparable, the exoergicity of the former case is significantly lower than that of the latter case. The above-mentioned conclusions are consistent with the results derived from the OH-initiated oxidation of $HOCH(CH_3)OOH$ from the *anti*-CH_3CHOO + H_2O reaction. Zhou et al. has demonstrated that the bimolecular reaction of *syn*-CH_3CHOO with water leading to the formation of $HOCH(CH_3)OOH$ is of less importance in the atmosphere, while the unimolecular decay to OH radical is the major loss process of *syn*-CH_3CHOO (Zhou et al., 2019). Therefore, in the present study, we mainly focus on the subsequent mechanism of intermediate generated from OH-initiated oxidation of $HOCH(CH_3)OOH$ from the *anti*-CH_3CHOO + H_2O reaction.

Figure S4. PES ($\Delta G_a^{\#}$) for the OH-initiated reactions of HOCH(CH$_3$)OOH from the *syn*-CH$_3$CHOO + H$_2$O reaction predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory (a and b represent the pre-reactive and post-reactive complexes)
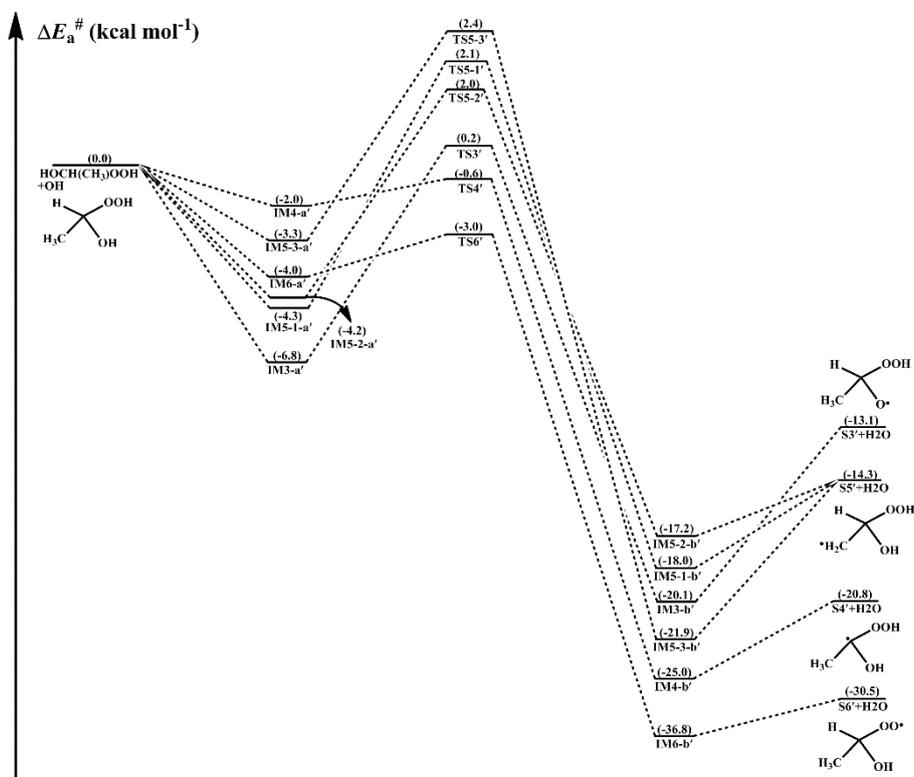
Figure S5. PES ($\Delta E_a^{\#}$) for the OH-initiated reactions of HOCH(CH$_3$)OOH from the *syn*-CH$_3$CHOO + H$_2$O reaction predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory (a and b represent the pre-reactive and post-reactive complexes)

Corresponding descriptions have been added in the page 11 line 289-308 of the revised manuscript:

For the OH-initiated oxidation of HOCH(CH₃)OOH from the syn-CH₃CHOO + H₂O reaction, the corresponding free-energy and electronic-energy PESs are displayed in Figures S4 and S5, respectively. From Figure S4, it can be seen the H-abstraction by OH radical from HOCH(CH₃)OOH has six kinds of pathways. For each pathway, a per-reactive complex is formed prior to the corresponding transition state, and then it overcomes modest barrier to reaction. The $\Delta G_a^{\#}$ of R6' and R8' are 2.3 and 1.8 kcal mol^{-1}, respectively, which are about 5 kcal mol^{-1} lower than those of R5' and R7'. This result shows that H-abstraction from the -CH (R6') and -OOH (R8') groups are preferable kinetically. Same conclusion is also derived from the energy barriers $\Delta E_a^{\#}$ that the R6' and R8' the most favourable H-abstraction pathways (Figure S5). It should be noted that although the barriers of R6' and R8' are comparable, the exoergicity of the former case is significantly lower than that of the latter case. The above-mentioned conclusions are consistent with the results derived from the OH-initiated oxidation of HOCH(CH₃)OOH from the anti-CH₃CHOO + H₂O reaction. Zhou et al. has demonstrated that the bimolecular reaction of syn-CH₃CHOO with water leading to the formation of HOCH(CH₃)OOH is of less importance in the atmosphere, while the unimolecular decay to OH radical is the major loss process of syn-CH₃CHOO (Zhou et al., 2019). Therefore, in the present study, we mainly focus on the subsequent mechanism of intermediate generated from OH-initiated oxidation of HOCH(CH₃)OOH from the anti-CH₃CHOO + H₂O reaction.

2. Line 226-228, the reaction barriers are reduced in the order of 6.4 (R1) > 5.8 (R3) ≈ 5.4 (R2) > 1.5 (R4) kcal mol^{-1}, indicating that H-abstraction from the -OOH group is the most favorable. The authors should explain the order of TS1, TS3, TS2, and TS4 in the initial H-abstraction reactions.

Response: Based on the Reviewer's suggestion, the corresponding explanations on the order of barrier heights of H-abstraction reactions have been added in the revised manuscript. A schematic PES for the initiation reactions of OH radical with $HOCH_2OOH$ is drawn in Figure 2. As can be seen in Figure 2, the reaction for $HOCH_2OOH$ with OH radical proceeds via four distinct pathways: H-abstraction from the $-O_1H_1$ (R1), $-C_1H_3$ (R2), $-C_1H_4$ (R3) and $-O_2O_3H_2$ groups (R4). For each pathway, a pre-reactive complex with a six- or seven-membered ring

structure is formed in the entrance channel, which is stabilized by hydrogen bond interactions between the oxygen atom of OH radical and the abstraction hydrogen atom of $HOCH_2OOH$, and the remnant hydrogen atom of OH radical and one of oxygen atoms of $HOCH_2OOH$. Then, it surmounts modest barrier that is higher in energy than the reactants to reaction. The reaction barrier $\Delta G_a^{\#}$ are reduced in the order of 6.4 (R1) > 5.8 (R2) ≈ 5.4 (R3) > 1.5 (R4) kcal mol^{-1}, indicating that H-abstraction from the $-O_2O_3H_2$ group (R4) is more preferable than those from the $-O_1H_1$, $-C_1H_3$ and $-C_1H_4$ groups (R1-R3). Same conclusion is also derived from the energy barriers $\Delta E_a^{\#}$ that R4 is the most favorable H-abstraction pathway (Figure S1). The difference of barrier heights can be attributed to the bond dissociation energy (BDE) of different types of bonds in $HOCH_2OOH$ molecule. The BDE are decreased in the order of 103.7 (O_1-H_1) > 98.2 (C_1-H_3) ≈ 97.4 (C_1-H_4) > 87.2 (O_3-H_2) kcal mol^{-1}, which are in good agreement with the order of barrier heights of H-abstraction reactions.

Figure 2. PES ($\Delta G_a^{\#}$) for the OH-initiated reactions of $HOCH_2OOH$ from the $CH_2OO + H_2O$ reaction predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory (a and b represent the pre-reactive and post-reactive complexes)
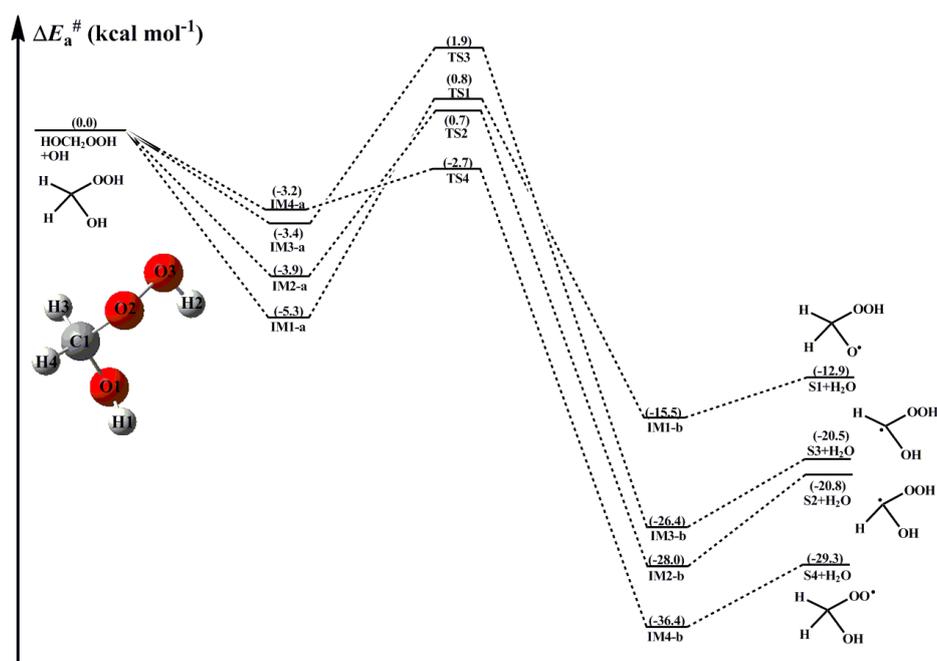
Figure S1. PES ($\Delta E_a^{\#}$) for the OH-initiated reactions of HOCH$_2$OOH from the CH$_2$OO + H$_2$O reaction predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory (a and b represent the pre-reactive and post-reactive complexes)

Corresponding descriptions have been added in the page 10 line 253-269 of the revised manuscript:

As can be seen in Figure 2, the reaction for HOCH$_2$OOH with OH radical proceeds via four distinct pathways: H-abstraction from the -O$_1$H$_1$ (R1), -C$_1$H$_3$ (R2), -C$_1$H$_4$ (R3) and -O$_2$O$_3$H$_2$ groups (R4). For each pathway, a pre-reactive complex with a six- or seven-membered ring structure is formed in the entrance channel, which is stabilized by hydrogen bond interactions between the oxygen atom of OH radical and the abstraction hydrogen atom of HOCH$_2$OOH, and the remnant hydrogen atom of OH radical and one of oxygen atoms of HOCH$_2$OOH. Then, it surmounts modest barrier that is higher in energy than the reactants to reaction. The reaction barrier $\Delta G_a^{\#}$ are reduced in the order of 6.4 (R1) > 5.8 (R2) ≈ 5.4 (R3) > 1.5 (R4) kcal mol^{-1}, indicating that H-abstraction from the -O$_2$O$_3$H$_2$ group (R4) is more preferable than those from the -O$_1$H$_1$, -C$_1$H$_3$ and -C$_1$H$_4$ groups (R1-R3). Same conclusion is also derived from the energy barriers $\Delta E_a^{\#}$ that R4 is the most favorable H-abstraction pathway (Figure S1). The difference of barrier heights can be attributed to the bond dissociation energy (BDE) of different types of bonds in HOCH$_2$OOH molecule. The BDE are decreased in the order of 103.7 (O$_1$-H$_1$) > 98.2 (C$_1$-H$_3$) ≈ 97.4 (C$_1$-H$_4$) > 87.2 (O$_3$-H$_2$) kcal mol^{-1}, which are in good agreement with the order of barrier heights of H-abstraction reactions.

3. The authors discuss the mechanism of RO_2 reactions with HO_2. But there is no information provided on HO_2. They must describe how HO_2 is formed in the atmosphere, what is its concentration, and where this reaction could be relevant.

Response: Based on the Reviewer's suggestion, the relevant information on the production of HO_2 radical has been added in the revised manuscript. The main sources of HO_2 radcial involve the photo-oxidation of oxygenated volatile organic compounds (OVOCs) and the ozonolysis reaction, as well as senondary sources include the reactions of OH radical with CO, ozone and volatile organic compounds (VOCs), the reaction of alkoxy radcial RO with O_2 and the red-light-induced decomposition of α-hydroxy methylperoxy radical $OHCH_2OO$ (Stone et al., 2012; Hofzumahaus et al., 2009; Kumar et al., 2015). The atmospheric concentration of HO_2 radical is 1.5-10 $\times 10^8$ molecules cm^{-3} at ground level in polluted urban environments (Stone et al., 2012).

Corresponding descriptions have been added in the page 21 line 496-503 of the revised manuscript:

The main sources of HO_2 radical involve the photo-oxidation of oxygenated volatile organic compounds (OVOCs) and the ozonolysis reaction, as well as senondary sources include the reactions of OH radical with CO, ozone and volatile organic compounds (VOCs), the reaction of alkoxy radical RO with O_2 and the red-light-induced decomposition of α-hydroxy methylperoxy radical $OHCH_2OO$ (Kumar et al., 2015; Stone et al., 2012; Hofzumahaus et al., 2009). The atmospheric concentration of HO_2 radical is 1.5-10 $\times 10^8$ molecules cm^{-3} at ground level in polluted urban environments (Stone et al., 2012).

4. Authors should compare $k_{\text{MC-TST}}$ and the pseudo first-order rates (k'_{HO2} and k'_{NO}) for the bimolecular processes (HO_2 reaction and NO reaction) as a function of concentration. See the recent review of autoxidation by Bianchi et al. (Chem. Rev. 2019, 119, 6, 3472-3509).

Response: As the Reviewer's said, the relative importance of different transformation pathways (unimolecular, $HO_2 \cdot$ and NO reactions) of peroxy radicals RO_2 is significantly dependent on the rate coefficients and coreactant concentrations. For the H-shift reaction of RO_2 radicals, the multi-conformer rate coefficient $k_{\text{MC-TST}}$ can be calculated by the weighted sum of the single-conformer rate coefficient $k_{\text{IRC-TST}}$. At room temperature, $k_{\text{MC-TST}}$ of first H-shift reaction of

HOCH$_2$OO radical is calculated to be 4.4 $\times$ 10^{-16} s^{-1}. The room temperature rate coefficient of HOCH$_2$OO radical reaction with HO$_2$ radical is estimated to be 1.7 $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}. The typical atmospheric concentrations of HO$_2$ radical are 5, 20 and 50 pptv in the urban, rural and forest environments (Bianchi et al., 2019), translating into the pseudo-first-order rate constants $k'_{HO2} = k_{HO2}[HO_2]$ of 1.1 $\times$ 10^{-3}, 4.2 $\times$ 10^{-3} and 1.1 $\times$ 10^{-2} s^{-1}, respectively.

The typical atmospheric concentrations of NO are about 10 ppbv, 1 ppbv and 20 pptv in the urban, rural and forest environments (Bianchi et al., 2019). The rate coefficient of HOCH$_2$OO radical reaction with NO is calculated to be 4.3 $\times$ 10^{-12} cm^3 molecule^{-1} s^{-1} at room temperature, resulting in the pseudo-first-order rate constants $k'_{NO} = k_{NO}[NO]$ of 6.5 $\times$ 10^{-1}, 6.5 $\times$ 10^{-2}, and 1.3 $\times$ 10^{-3}, respectively, in the urban, rural and forest environments. It is of interest to assess the relative importance for the H-shift reaction of HOCH$_2$OO radical and bimolecular reactions with HO$_2$ ·and NO based on the calculated k_{MC-TST}, k'_{HO2} and k'_{NO}. It can be found that the H-shift reaction is of less importance, the HO$_2$ radical reaction is favourable in the forest environment, the NO reaction is predominant in the urban and rural regions. Similar conclusion is also obtained from the cases of HOCH(CH$_3$)OO and HO(CH$_3$)$_2$CHOO radicals.

Corresponding descriptions have been added in the page 22 line 525-531 and page 27 line 653-664 of the revised manuscript:

At ambient temperature, k_{R31} is estimated to be 1.7 $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1}, which is in good agreement with the value of ~2 $\times$ 10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of acyl peroxy radicals with HO$_2$ radical (Wennberg et al., 2018). The typical atmospheric concentrations of HO$_2$ radical are about 5, 20 and 50 pptv in the urban, rural and forest environments (Bianchi et al., 2019), translating into the pseudo-first-order rate constants $k'_{HO2} = k_{HO2}[HO_2]$ of 1.1 $\times$ 10^{-3}, 4.2 $\times$ 10^{-3} and 1.1 $\times$ 10^{-2} s^{-1}, respectively.

The typical atmospheric concentrations of NO are about 10 ppbv, 1 ppbv and 20 pptv in the urban, rural and forest environments (Bianchi et al., 2019). The rate coefficient of HOCH$_2$OO · reaction with NO is calculated to be 4.3 $\times$ 10^{-12} cm^3 molecule^{-1} s^{-1} at room temperature, resulting in the pseudo-first-order rate constants $k'_{NO} = k_{NO}[NO]$ of 6.5 $\times$ 10^{-1}, 6.5 $\times$ 10^{-2}, and 1.3 $\times$ 10^{-3}, respectively, in the urban, rural and forest environments. It is of interest to assess the relative importance for the H-shift reaction of HOCH$_2$OO radical and bimolecular reactions with HO$_2$ ·and NO based on the calculated k_{MC-TST}, k'_{HO2} and k'_{NO}. It can be found that

the H-shift reaction is of less importance, the HO₂ radical reaction is favorable in the forest environment, while the NO reaction is predominant in the urban and rural regions. Similar conclusion is also obtained from the cases of HOCH(CH₃)OO and HO(CH₃)₂CHOO radicals.

5. For the alkoxy radical fragmentation, the author should calculate rate constants in the temperature range studied.

Response: Based on the Reviewer's suggestion, the rate coefficients of the dominant pathways of alkoxyl radical fragmentation have been calculated over the temperature range of 273-400 K. The corresponding results are listed in Table S12 of the revised manuscript. For the fragmentation of $HOCH_2O$ radical, the dominant pathway is H-abstraction by O_2 from $HOCH_2O$ radical resulting in formation of HCOOH and HO_2 radical (R41). For the fragmentation of $HOCH(CH_3)O$ and $HOC(CH_3)_2O$ radicals, the dominant pathways are β-site C-C bond scission leading to the formation of HCOOH + $CH_3 \cdot$ (R45) and $CH_3COOH + CH_3 \cdot$ (R51). As can be seen in Table S12, k_{R41} is slightly increased with the temperature increasing, and the discrepancy is about a factor of 12 at the two extremes of temperature. At ground level with $[O_2] = \sim 5.0 \times 10^{18}$ molecule cm^{-3}, the pseudo-first-order rate constant $k'_{O2} = k_{R41}[O_2]$ is estimated to be 38.0 s^{-1} at room temperature. k_{R45} vary significantly from 2.0×10^6 (273 K) to 3.1×10^8 (400 K) s^{-1}, and they exhibit a marked positive temperature dependence. Similar phenomenon is also observed from k_{R51} that k_{R51} is significantly increased with the temperature increasing. k_{R51} is a factor of ~ 1.3 greater than k_{R45} in the temperature range studied, implying that the rate coefficient of β-site C-C bond scission is slightly increased as the number of methyl group is increased.

Table S12 Rate coefficients of the dominant pathways of the fragmentation of $HOCH_2O \cdot$ (R41), $HOCH(CH_3)O \cdot$ (R45) and $HO(CH_3)_2CO \cdot$ (R51) computed at different temperatures

T/K	k_{R41}(cm³ molecule⁻¹ s⁻¹)	k_{R45}(s⁻¹)	k_{R51}(s⁻¹)
273	4.3×10^{-18}	2.0×10^6	2.6×10^6
280	5.0×10^{-18}	2.9×10^6	3.8×10^6
298	7.6×10^{-18}	7.3×10^6	9.5×10^6
300	7.9×10^{-18}	8.1×10^6	1.0×10^7
320	1.2×10^{-17}	1.9×10^7	2.5×10^7
340	1.8×10^{-17}	4.4×10^7	5.6×10^7
360	2.6×10^{-17}	9.0×10^7	1.1×10^8

380	3.7×10^{-17}	1.7×10^8	2.2×10^8
400	5.1×10^{-17}	3.1×10^8	3.8×10^8

Corresponding descriptions have been revised in the page 26 line 625-629, page 27 line 633-640, page 27 line 648-652 and page 28 line 655-675 of the revised manuscript:

The formed $HOCH_2O$ radical has two kinds of pathways: (1) it directly decomposes into CH_2O and OH radical (R40) via β-site C_1-O_1 bond scission with the barrier of 52.4 kcal mol^{-1}; (2) it converts into HCOOH and HO_2 radical (R41) through H-abstraction by O_2 with the barrier of 26.4 kcal mol^{-1}. This result reveals that R41 is the most feasible channel in the fragmentation of $HOCH_2O$ radical.

The resulting $HOCH(CH_3)O$ radical has three types of pathways. The first one is β-site C_1-C_2 bond scission leading to the formation of HCOOH + CH_3 (R45) with the barrier of 8.3 kcal mol^{-1}. The second one is β-site C_1-O_1 bond cleavage resulting in formation of CH_3COH + OH (R46) with the barrier of 26.7 kcal mol^{-1}. The third one is H-abstraction by O_2 leading to CH_3COOH + HO_2 ·(R47) with the barrier of 26.2 kcal mol^{-1}. Based on the calculated reaction barriers, it can be found that β-site C_1-C_2 bond scission is the dominant pathway in the fragmentation of $HOCH(CH_3)O$ radical.

The formed $HO(CH_3)_2CO$ radical can either dissociate to CH_3COOH + CH_3 ·(R51) via the C_1-C_3 bond scission with the barrier of 8.2 kcal mol^{-1}, or decompose into CH_3COCH_3 + OH (R52) through the C_1-O_1 bond breaking with the barrier of 24.3 kcal mol^{-1}. The result again shows that the β-site C-C bond scission is the dominate pathway.

The rate coefficients of the dominant pathways of $HOCH_2O$, $HOCH(CH_3)O$ and $HO(CH_3)_2CHO$ radicals fragmentation are summarized in Table S12. As can be seen in Table S12, k_{R41} is slightly increased with the temperature increasing, and the discrepancy is about a factor of 12 at the two extremes of temperature. At ground level with $[O_2] = \sim 5.0 \times 10^{18}$ molecule cm^{-3}, the pseudo-first-order rate constant $k'_{O2} = k_{R41}[O_2]$ is estimated to be 38.0 s^{-1} at room temperature. k_{R45} vary significantly from 2.0×10^6 (273 K) to 3.1×10^8 (400 K) s^{-1}, and they exhibit a marked positive temperature dependence. Similar phenomenon is also observed from k_{R51} that k_{R51} is significantly increased with increasing temperature. k_{R51} is a factor of ~ 1.3 greater than k_{R45} in the temperature range studied, implying that the rate coefficient of β-site C-C bond scission is slightly increased as the number of methyl group is increased.

6. The prefix 'anti' should be italicized throughout the manuscript.

   Response: Based on the Reviewer's suggestion, the prefix 'anti' is italicized throughout the manuscript.

7. The italics/non-italics energies in Fig. S13 and S14 in the supplement are not always in the same vertical order.

   Response: Based on the Reviewer's suggestion, the non-italics energies have been placed in the upper number in Figures S13 and S14.
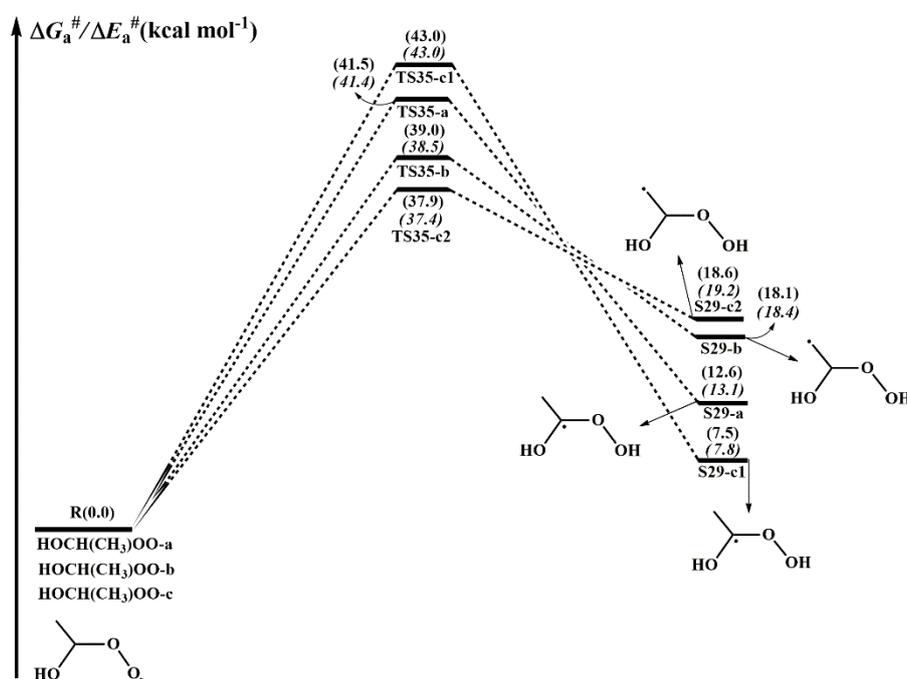
Figure S13. PES ($\Delta G_a^{\#}$ and $\Delta E_a^{\#}$, in italics) for the autoxidation of $HOCH_3CHOO$ radical predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory
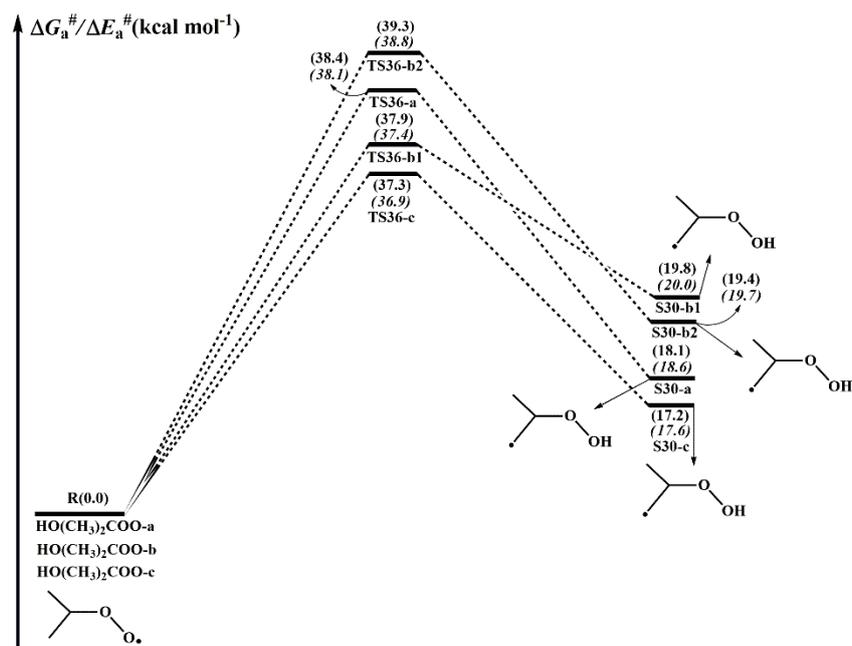
Figure S14. PES ($\Delta G_a^{\#}$ and $\Delta E_a^{\#}$, in italics) for the autoxidation of HO(CH$_3$)$_2$COO radical predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory

8. There are some grammatical and logical errors in this manuscript. I suggest revising the grammatical errors accordingly.

   Response: Based on the Reviewer's suggestion, the sentences/phrases, missing words, and the grammatically confusing sentences have been corrected carefully in the revised manuscript.

References

1. Zhou, X., Liu, Y., Dong, W., and Yang, X.: Unimolecular reaction rate measurement of *syn*-CH$_3$CHOO, J. Phys. Chem. Lett., 10, 4817-4821, https://doi.org/10.1021/acs.jpclett.9b01740, 2019.

2. Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO$_2$ radicals: field measurements and model comparisons, Chem. Soc. Rev., 41, 6348-6404, https://doi.org/10.1039/c2cs35140d, 2012.

3. Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified trace gas removal in the troposphere, Science, 324, 1702-1704, https://doi.org/10.1126/science.1164566, 2009.

4. Kumar, M., and Francisco, J. S.: Red-light-induced decomposition of an organic peroxy radical: a new source of the HO$_2$ radical, Angew. Chem. Int. Ed., 54, 15711-15714, https://doi.org/10.1002/anie.201509311, 2015.

5. Bianchi, F., Kurten, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J. D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly oxygenated organic molecules (HOM) from gas-phase autoxidation involving peroxy radicals: a key contributor to atmospheric aerosol, Chem. Rev., 119, 3472-3509, https://doi.org/10.1021/acs.chemrev.8b00395, 2019.