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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 #2

1. Authors discuss the transformation mechanism of HHPs. But there is no information on the concentration of HHPs (in forested regions?).

   Response: Based on the Reviewer's suggestion, the concentrations of hydroxyalkyl hydroperoxides (HHPs) have been added in the revised manuscript. Hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$), the simplest HHPs from the ozonolysis of ethene in the presence of water, is observed in significant abundance in the atmosphere (Allen et al., 2018). The measured concentration of HMHP is varied considerably depending on the location, season and altitude, and its concentration is measured to be up to 5 ppbv in forested regions (Allen et al., 2018; Francisco and Eisfeld, 2009). Recently, the concentration of HMHP was measured during the summer 2013 in the southeastern United States, and found that the average mixing ratio of HMHP is 0.25 ppbv with a maximum of 4.0 ppbv in the boundary layer (Allen et al., 2018).

   Corresponding descriptions have been added in the page 4 line 98-106 of the revised manuscript:

   Hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$), the simplest HHPs from the ozonolysis of ethene in the presence of water, is observed in significant abundance in the atmosphere (Allen et al., 2018). The measured concentration of HMHP is varied considerably depending on the location, season and altitude, and its concentration is measured to be up to 5 ppbv in forested regions (Allen et al., 2018; Francisco and Eisfeld, 2009). Recently, the concentration of HMHP was measured during the summer 2013 in the southeastern United States, and found that the average mixing ratio of HMHP is 0.25 ppbv with a maximum of 4.0 ppbv in the boundary layer(Allen et al., 2018).

2. The lifetimes of distinct HHPs with respect to OH should be estimated under atmospheric conditions.

   Response: Based on the Reviewer's suggestion, the lifetime of distinct HHPs reactivity toward OH radical has been added in the revised manuscript. The atmospheric lifetime is expressed as eqn (1): (Long et al., 2017)

$$\tau = \frac{1}{k[\text{X}]} \tag{1}$$

where k is the rate coefficient of distinct HHPs reactions with OH radical. [X] is the concentration of OH radical, which varies from 5 to 15×10^6 molecules cm^{-3} during daylight (Tan et al., 2017). At ambient temperature, the total rate coefficients of OH radical reactions with HOCH$_2$OOH, HOCH(CH$_3$)OOH and HOC(CH$_3$)$_2$OOH are 3.3×10^{-11}, 3.0×10^{-11} and 1.6×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. The atmospheric lifetime of HOCH$_2$OOH, HOCH(CH$_3$)OOH and HOC(CH$_3$)$_2$OOH reactivity toward OH radical are estimated to be 0.58-1.74 h, 0.60-1.79 h and 1.23-3.69 h at room temperature.

Corresponding descriptions have been added in the page 13 line 348-352 of the revised manuscript:

The concentrations of OH radical vary from 5 to 15×10^6 molecules cm^{-3} during daylight (Long et al., 2017), resulting in the atmospheric lifetime of HOCH$_2$OOH, HOCH(CH$_3$)OOH and HOC(CH$_3$)$_2$OOH reactivity toward OH radical are estimated to be 0.58-1.74 h, 0.60-1.79 h and 1.23-3.69 h at room temperature.

3. $\Delta E_a^{\#}$, $\Delta G_a^{\#}$ and ΔG are employed in the manuscript, the author should explain the meaning of each item in detail.

Response: Based on the Reviewer's suggestion, the explanations on the meaning of $\Delta E_a^{\#}$, $\Delta G_a^{\#}$ and ΔG have been added in the revised manuscript. The Gibbs free energy (G) for each species is obtained by combining the single-point energy with the Gibbs correction ($G = G_{corr} + E$). The electronic energy ($\Delta E_a^{\#}$) and free energy ($\Delta G_a^{\#}$) barriers are defined as the difference in energy between transition state and pre-reactive complex ($\Delta E_a^{\#} = E_{TS} - E_{RC}$ and $\Delta G_a^{\#} = G_{TS} - G_{RC}$). The reaction free energy (ΔG) is referred to the difference in energy between product and reactant ($\Delta G = G_P - G_R$).

Corresponding descriptions have been added in the page 7 line 178-183 of the revised manuscript:

Herein, the Gibbs free energy (G) for each species is obtained by combining the single-point energy with the Gibbs correction ($G = G_{corr} + E$). The electronic energy ($\Delta E_a^{\#}$) and free energy ($\Delta G_a^{\#}$) barriers are defined as the difference in energy between transition state and pre-reactive complex ($\Delta E_a^{\#} = E_{TS} - E_{RC}$ and $\Delta G_a^{\#} = G_{TS} - G_{RC}$). The reaction free energy (ΔG) is referred to the difference in energy between product and reactant ($\Delta G = G_P - G_R$).

4. Author should compare the barriers of the gas phase decomposition of HOCH$_2$OO radical with the barrier of self-reaction of HOCH$_2$OO radical. Kumar and Francisco reported the unimolecular decay of HOCH$_2$OO radical could be a new source of HO2 radical (Angew. Chem. Int. Ed. 2015, 54, 15711-15714; J. Phys. Chem. A 2016, 120, 2677-2683).

Response: Based on the Reviewer's suggestion, the comparation on the barriers of the gas phase decomposition of HOCH$_2$OO radical and its self-reaction has been added in the revised manuscript. As can be seen in Figure 5, the self-reaction of HOCH$_2$OO radical proceeds via oxygen-to-oxygen coupling leading to the formation of tetroxide intermediate S14 with the electronic energy and free energy barriers of 7.3 and 19.6 kcal mol^{-1}. Kumar and Francisco reported that the electronic energy barrier of the gas phase decomposition of HOCH$_2$OO radical is 14.0 kcal mol^{-1} and it could be a new source of HO$_2$ radical in the troposphere (Kumar and Francisco, 2015, 2016). Compared with the electronic energy barriers of unimolecular decomposition of HOCH$_2$OO radical and its self-reaction, it can be found that the self-reaction of HOCH$_2$OO radical resulting in formation of tetroxide intermediate S14 is significantly feasible. The related reference has been cited in the revised manuscript.

Corresponding descriptions have been added in the page 16 line 412-420 of the revised manuscript:

The self-reaction of HOCH$_2$OO radical proceeds via oxygen-to-oxygen coupling leading to the formation of tetroxide intermediate S14 with the electronic energy and free energy barriers of 7.3 and 19.6 kcal mol^{-1}. Kumar and Francisco reported that the electronic energy barrier of the gas phase decomposition of HOCH$_2$OO radical is 14.0 kcal mol^{1} and it could be a new source of HO$_2$ radical in the troposphere (Kumar and Francisco, 2015, 2016). Compared with the electronic energy barriers of unimolecular dissociation of HOCH$_2$OO radical and its self-reaction, it can be found that the self-reaction of HOCH$_2$OO radical resulting in formation of S14 is significantly feasible.

5. Author should provide the pseudo first order rates for the reactions of distinct RO$_2$ radicals with HO$_2$ and NO under the urban, rural and forest environments.

Response: Based on the Reviewer's suggestion, the pseudo-first-order rate constants of

distinct RO_2 radicals reactions with HO_2 radical and NO have been added in the revised manuscript. 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). At ambient temperature, the rate coefficient k_{R31} of $HOCH_2OO \cdot + HO_2 \cdot$ reaction (R31) is estimated to be 1.7×10^{-11} cm^3 molecule^{-1} s^{-1}, translating into the pseudo-first-order rate constants $k'_{HO2} = k_{HO2}[HO_2]$ of 1.1×10^{-3}, 4.2×10^{-3} and 1.1×10^{-2} s^{-1}, respectively, in the urban, rural and forest environments. The pseudo-first-order rate constants of $HOCH(CH_3)OO \cdot + HO_2 \cdot$ (R32) and $HOC(CH_3)_2OO \cdot + HO_2 \cdot$ (R33) reactions are predicted to be 3.0×10^{-3} and 4.8×10^{-3} (urban), 1.1×10^{-2} and 1.8×10^{-2} (rural), 3.0×10^{-2} and 4.8×10^{-2} s^{-1} (forest) at room temperature.

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 k_{R39} of $HOCH_2OO$ radical reaction with NO is estimated to be 4.3×10^{-12} cm^3 molecule^{-1} s^{-1} at ambient temperature, resulting in the pseudo-first-order rate constants $k'_{NO} = k_{NO}[NO]$ of 6.5×10^{-1}, 6.5×10^{-2}, and 1.3×10^{-3}, respectively, in the urban, rural and forest environments. For the bimolecular reaction of $HOCH(CH_3)OO$ radical with NO, the predicted pseudo-first-order rate constants are 6.7×10^{-1}, 6.7×10^{-2}, and 1.3×10^{-3}, respectively, in the urban, rural and forest environments. The pseudo-first-order rate constants of $HOC(CH_3)_2OO$ radical reaction with NO are 7.3×10^{-1}, 7.3×10^{-2}, and 1.5×10^{-3}, respectively, in the urban, rural and forest environments.

Corresponding descriptions have been added in the page 22 line 525-533 and page 27 line 653-658 of the revised manuscript:

At ambient temperature, k_{R31} is estimated to be 1.7×10^{-11} cm^3 molecule^{-1} s^{-1}, which is in good agreement with the value of $\sim 2 \times 10^{-11}$ 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 1.1×10^{-3}, 4.2×10^{-3} and 1.1×10^{-2} s^{-1}, respectively. The pseudo-first-order rate constants of R32 and R33 are predicted to be 3.0×10^{-3} and 4.8×10^{-3} (urban), 1.1×10^{-2} and 1.8×10^{-2} (rural), 3.0×10^{-2} and 4.8×10^{-2} s^{-1} (forest) at room temperature.

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

HOCH₂OO · reaction with NO is calculated to be 4.3 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ at room temperature, resulting in the pseudo-first-order rate constants k'_NO = k_NO[NO] of 6.5 × 10⁻¹, 6.5 × 10⁻², and 1.3 × 10⁻³, respectively, in the urban, rural and forest environments. For the bimolecular reaction of HOCH(CH₃)OO radical with NO, the predicted pseudo-first-order rate constants are 6.7 × 10⁻¹, 6.7 × 10⁻², and 1.3 × 10⁻³, respectively, in the urban, rural and forest environments. The pseudo-first-order rate constants of HOC(CH₃)₂OO radical reaction with NO are 7.3 × 10⁻¹, 7.3 × 10⁻², and 1.5 × 10⁻³, respectively, in the urban, rural and forest environments.

6. In Fig. 2, the text (mentioned structural parameters) overlaps with the structures.

Response: Based on the Reviewer's suggestion, the Figure 2 has been redrawn in the revised manuscript. For clarity, the 2D drawings of some important species are labeled in Figure 2. The optimized geometries of all the stationary points involved in the initial reactions of OH radical with $HOCH_2OOH$ are displayed Figure S6.
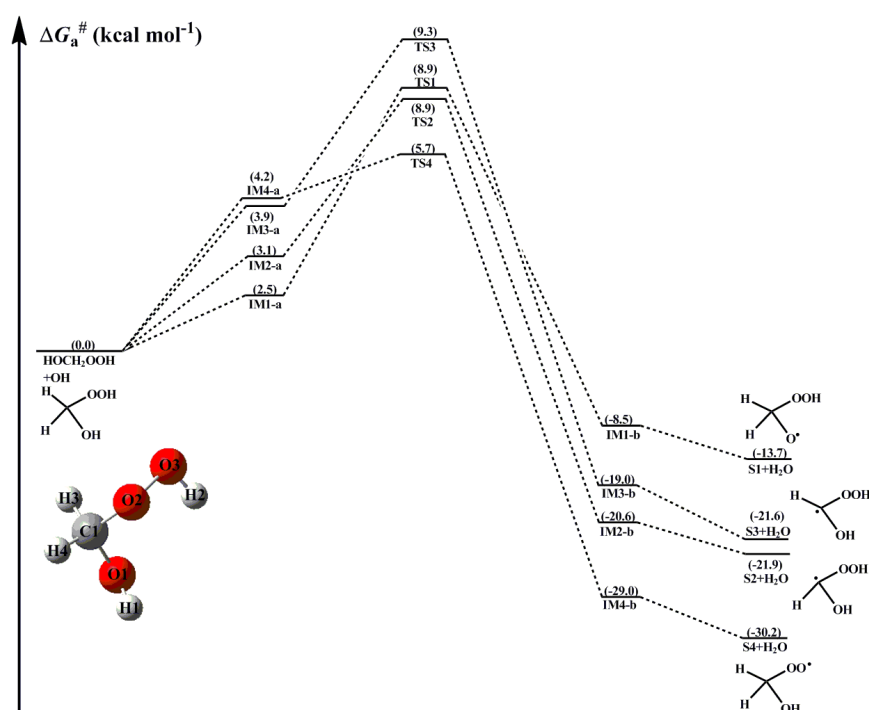
Figure 2. PES ($\Delta G_a^{\#}$) for the OH-initiated reactions of $HOCH_2OOH$ from the $CH_2OO + H_2O$ reaction predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory (a and b represent the pre-reactive and post-reactive complexes)
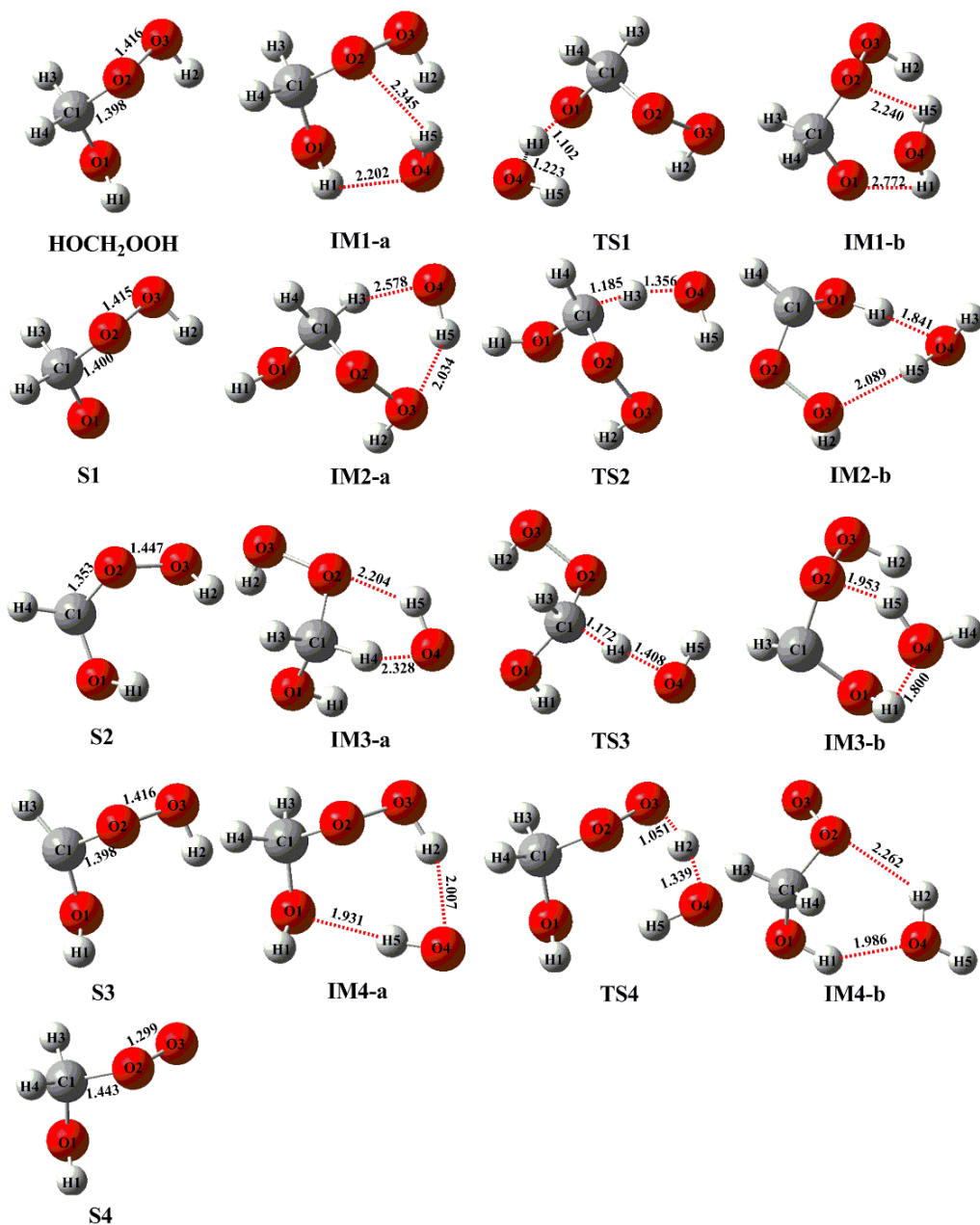
Figure S6. Geometries of all the stationary points for the initial reaction of HOCH$_2$OOH with OH radical optimized at the M06-2X/6-311+G(2df,2p) level of theory

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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.

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