

Atmos. Chem. Phys. Discuss., author comment AC1  
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## Reply on RC1

Long Chen et al.

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Author comment on "OH-initiated atmospheric degradation of hydroxyalkyl hydroperoxides: mechanism, kinetics, and structure–activity relationship" by Long Chen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-890-AC1>, 2022

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Jan. 27, 2022

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

- The investigated HHPs are generated from the reactions of  $\text{CH}_2\text{OO}$ , *anti*- $\text{CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  with water vapor, not considering the HHP from the bimolecular reaction of *syn*- $\text{CH}_3\text{CHOO}$  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*- $\text{CH}_3\text{CHOO}$  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  $\text{HOCH}(\text{CH}_3)\text{OOH}$  has six kinds of pathways. For each pathway, a pre-reactive complex is formed prior to the corresponding transition state, and then it overcomes modest barrier to reaction. The  $\Delta G_a^\ddagger$  of R6' and R8' are 2.3 and 1.8  $\text{kcal}\cdot\text{mol}^{-1}$ , respectively, which are  $\sim 5 \text{ kcal}\cdot\text{mol}^{-1}$  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  $\Delta E_a^\ddagger$  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  $\text{HOCH}(\text{CH}_3)\text{OOH}$  from the *anti*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$  reaction. Zhou et al. has demonstrated that the bimolecular reaction of *syn*- $\text{CH}_3\text{CHOO}$  with water leading to the formation of  $\text{HOCH}(\text{CH}_3)\text{OOH}$  is of less importance in the atmosphere, while the unimolecular decay to OH radical is the major loss process of *syn*- $\text{CH}_3\text{CHOO}$  (Zhou et al., 2019). Therefore, in the present study, we mainly focus on the subsequent mechanism of intermediate generated from OH-initiated oxidation of  $\text{HOCH}(\text{CH}_3)\text{OOH}$  from the *anti*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$  reaction.

**Figure S4.** PES ( $\Delta G_a^\ddagger$ ) for the OH-initiated reactions of  $\text{HOCH}(\text{CH}_3)\text{OOH}$  from the *syn*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$  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 ( $\Delta E_a^\ddagger$ ) for the OH-initiated reactions of  $\text{HOCH}(\text{CH}_3)\text{OOH}$  from the *syn*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$  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  $\text{HOCH}(\text{CH}_3)\text{OOH}$  from the *syn*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$  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  $\text{HOCH}(\text{CH}_3)\text{OOH}$  has six kinds of pathways. For each pathway, a pre-reactive complex is formed prior to the corresponding transition state, and then it overcomes modest barrier to reaction. The  $\Delta G_a^\ddagger$  of R6' and R8' are 2.3 and 1.8  $\text{kcal}\cdot\text{mol}^{-1}$ , respectively, which are about 5  $\text{kcal}\cdot\text{mol}^{-1}$  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  $\Delta E_a^\ddagger$  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(CH<sub>3</sub>)OOH from the anti-CH<sub>3</sub>CHOO + H<sub>2</sub>O reaction. Zhou et al. has demonstrated that the bimolecular reaction of syn-CH<sub>3</sub>CHOO with water leading to the formation of HOCH(CH<sub>3</sub>)OOH is of less importance in the atmosphere, while the unimolecular decay to OH radical is the major loss process of syn-CH<sub>3</sub>CHOO (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<sub>3</sub>)OOH from the anti-CH<sub>3</sub>CHOO + H<sub>2</sub>O reaction.

- 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<sup>-1</sup>, 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<sub>2</sub>OOH is drawn in Figure 2. As can be seen in Figure 2, the reaction for HOCH<sub>2</sub>OOH with OH radical proceeds via four distinct pathways: H-abstraction from the -O<sub>1</sub>H<sub>1</sub> (R1), -C<sub>1</sub>H<sub>3</sub> (R2), -C<sub>1</sub>H<sub>4</sub> (R3) and -O<sub>2</sub>O<sub>3</sub>H<sub>2</sub> 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<sub>2</sub>OOH, and the remnant hydrogen atom of OH radical and one of oxygen atoms of HOCH<sub>2</sub>OOH. Then, it surmounts modest barrier that is higher in energy than the reactants to reaction. The reaction barrier  $\Delta G_a^\ddagger$  are reduced in the order of 6.4 (R1) > 5.8 (R2) ≈ 5.4 (R3) > 1.5 (R4) kcal·mol<sup>-1</sup>, indicating that H-abstraction from the -O<sub>2</sub>O<sub>3</sub>H<sub>2</sub> group (R4) is more preferable than those from the -O<sub>1</sub>H<sub>1</sub>, -C<sub>1</sub>H<sub>3</sub> and -C<sub>1</sub>H<sub>4</sub> groups (R1-R3). Same conclusion is also derived from the energy barriers  $\Delta E_a^\ddagger$  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<sub>2</sub>OOH molecule. The BDE are decreased in the order of 103.7 (O<sub>1</sub>-H<sub>1</sub>) > 98.2 (C<sub>1</sub>-H<sub>3</sub>) ≈ 97.4 (C<sub>1</sub>-H<sub>4</sub>) > 87.2 (O<sub>3</sub>-H<sub>2</sub>) kcal·mol<sup>-1</sup>, which are in good agreement with the order of barrier heights of H-abstraction reactions.

**Figure 2.** PES ( $\Delta G_a^\ddagger$ ) for the OH-initiated reactions of HOCH<sub>2</sub>OOH from the CH<sub>2</sub>OO + H<sub>2</sub>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 S1.** PES ( $\Delta E_a^\ddagger$ ) for the OH-initiated reactions of HOCH<sub>2</sub>OOH from the CH<sub>2</sub>OO + H<sub>2</sub>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<sub>2</sub>OOH with OH radical proceeds via four distinct pathways: H-abstraction from the -O<sub>1</sub>H<sub>1</sub> (R1), -C<sub>1</sub>H<sub>3</sub> (R2), -C<sub>1</sub>H<sub>4</sub> (R3) and -O<sub>2</sub>O<sub>3</sub>H<sub>2</sub> 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<sub>2</sub>OOH, and the remnant hydrogen atom of OH radical and one of oxygen atoms of HOCH<sub>2</sub>OOH. Then, it surmounts modest barrier that is higher in energy than the reactants to reaction. The reaction barrier  $\Delta G_a^\ddagger$  are reduced in the order of 6.4 (R1) > 5.8 (R2)  $\approx$  5.4 (R3) > 1.5 (R4) kcal·mol<sup>-1</sup>, indicating that H-abstraction from the -O<sub>2</sub>O<sub>3</sub>H<sub>2</sub> group (R4) is more preferable than those from the -O<sub>1</sub>H<sub>1</sub>, -C<sub>1</sub>H<sub>3</sub> and -C<sub>1</sub>H<sub>4</sub> groups (R1-R3). Same conclusion is also derived from the energy barriers  $\Delta E_a^\ddagger$  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<sub>2</sub>OOH molecule. The BDE are decreased in the order of 103.7 (O<sub>1</sub>-H<sub>1</sub>) > 98.2 (C<sub>1</sub>-H<sub>3</sub>)  $\approx$  97.4 (C<sub>1</sub>-H<sub>4</sub>) > 87.2 (O<sub>3</sub>-H<sub>2</sub>) kcal·mol<sup>-1</sup>, which are in good agreement with the order of barrier heights of H-abstraction reactions.

- The authors discuss the mechanism of RO<sub>2</sub> reactions with HO<sub>2</sub>. But there is no information provided on HO<sub>2</sub>. They must describe how HO<sub>2</sub> 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<sub>2</sub> radical has been added in the revised manuscript. The main sources of HO<sub>2</sub> radical involve the photo-oxidation of oxygenated volatile organic compounds (OVOCs) and the ozonolysis reaction, as well as secondary sources include the reactions of OH radical with CO, ozone and volatile organic compounds (VOCs), the reaction of alkoxy radical RO with O<sub>2</sub> and the red-light-induced decomposition of  $\alpha$ -hydroxy methylperoxy radical OHCH<sub>2</sub>OO (Stone et al., 2012; Hofzumahaus et al., 2009; Kumar et al., 2015). The atmospheric concentration of HO<sub>2</sub> radical is 1.5-10 × 10<sup>8</sup> molecules cm<sup>-3</sup> 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<sub>2</sub> radical involve the photo-oxidation of oxygenated volatile organic compounds (OVOCs) and the ozonolysis reaction, as well as secondary sources include the reactions of OH radical with CO, ozone and volatile organic compounds (VOCs), the reaction of alkoxy radical RO with O<sub>2</sub> and the red-light-induced decomposition of  $\alpha$ -hydroxy methylperoxy radical OHCH<sub>2</sub>OO (Kumar et al., 2015; Stone et al., 2012; Hofzumahaus et al., 2009). The atmospheric concentration of HO<sub>2</sub> radical is 1.5-10 × 10<sup>8</sup> molecules cm<sup>-3</sup> at ground level in polluted urban environments (Stone et al., 2012).*

- Authors should compare  $k_{MC-TST}$  and the pseudo first-order rates ( $k'_{HO_2}$  and  $k'_{NO}$ ) for the bimolecular processes (HO<sub>2</sub> 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<sub>2</sub>· and NO reactions) of peroxy radicals RO<sub>2</sub> is significantly dependent on the rate coefficients and coreactant concentrations. For the H-shift reaction of RO<sub>2</sub> radicals, the multi-conformer rate coefficient  $k_{MC-TST}$  can be calculated by the weighted sum of the single-conformer rate coefficient  $k_{IRC-TST}$ . At room temperature,  $k_{MC-TST}$  of first H-shift reaction of HOCH<sub>2</sub>OO radical is calculated to be 4.4 × 10<sup>-16</sup> s<sup>-1</sup>. The room temperature rate coefficient of HOCH<sub>2</sub>OO radical reaction with HO<sub>2</sub> radical is estimated to be 1.7 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The typical atmospheric concentrations of HO<sub>2</sub> 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

$k'_{\text{HO}_2} = k_{\text{HO}_2}[\text{HO}_2]$  of  $1.1 \times 10^{-3}$ ,  $4.2 \times 10^{-3}$  and  $1.1 \times 10^{-2} \text{ s}^{-1}$ , 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<sub>2</sub>OO radical reaction with NO is calculated to be  $4.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature, resulting in the pseudo-first-order rate constants  $k'_{\text{NO}} = k_{\text{NO}}[\text{NO}]$  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<sub>2</sub>OO radical and bimolecular reactions with HO<sub>2</sub>· and NO based on the calculated  $k_{\text{MC-TST}}$ ,  $k'_{\text{HO}_2}$  and  $k'_{\text{NO}}$ . It can be found that the H-shift reaction is of less importance, the HO<sub>2</sub> 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<sub>3</sub>)OO and HO(CH<sub>3</sub>)<sub>2</sub>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,  $k_{\text{R31}}$  is estimated to be  $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is in good agreement with the value of  $\sim 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of acyl peroxy radicals with HO<sub>2</sub> radical (Wennberg et al., 2018). The typical atmospheric concentrations of HO<sub>2</sub> 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  $k'_{\text{HO}_2} = k_{\text{HO}_2}[\text{HO}_2]$  of  $1.1 \times 10^{-3}$ ,  $4.2 \times 10^{-3}$  and  $1.1 \times 10^{-2} \text{ s}^{-1}$ , 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<sub>2</sub>OO· reaction with NO is calculated to be  $4.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature, resulting in the pseudo-first-order rate constants  $k'_{\text{NO}} = k_{\text{NO}}[\text{NO}]$  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<sub>2</sub>OO radical and bimolecular reactions with HO<sub>2</sub>· and NO based on the calculated  $k_{\text{MC-TST}}$ ,  $k'_{\text{HO}_2}$  and  $k'_{\text{NO}}$ . It can be found that the H-shift reaction is of less importance, the HO<sub>2</sub> 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(CH<sub>3</sub>)OO and HO(CH<sub>3</sub>)<sub>2</sub>CHOO radicals.*

- 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 alkoxy 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<sub>2</sub>O radical, the dominant pathway is H-abstraction by O<sub>2</sub> from HOCH<sub>2</sub>O radical resulting in formation of HCOOH and HO<sub>2</sub> radical (R41). For the fragmentation of HOCH(CH<sub>3</sub>)O and HOC(CH<sub>3</sub>)<sub>2</sub>O radicals, the dominant pathways are β-site C-C bond scission leading to the formation of HCOOH + CH<sub>3</sub>· (R45) and CH<sub>3</sub>COOH + CH<sub>3</sub>· (R51). As can be seen in Table S12,  $k_{\text{R41}}$  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  $[\text{O}_2] = \sim 5.0 \times 10^{18} \text{ molecule cm}^{-3}$ , the pseudo-first-order rate constant  $k'_{\text{O}_2} = k_{\text{R41}}[\text{O}_2]$  is estimated to be  $38.0 \text{ s}^{-1}$  at room temperature.  $k_{\text{R45}}$  vary significantly from  $2.0 \times 10^6$  (273 K) to  $3.1 \times 10^8$  (400 K)  $\text{s}^{-1}$ , and they exhibit a marked positive temperature dependence. Similar phenomenon is also observed from  $k_{\text{R51}}$  that  $k_{\text{R51}}$  is significantly increased with the temperature increasing.  $k_{\text{R51}}$  is a factor of  $\sim 1.3$  greater than  $k_{\text{R45}}$  in the temperature range studied, implying that the

rate coefficient of  $\beta$ -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<sub>2</sub>O· (R41), HOCH(CH<sub>3</sub>)O· (R45) and HO(CH<sub>3</sub>)<sub>2</sub>CO· (R51) computed at different temperatures

T/K	$k_{R41}(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$k_{R45}(\text{s}^{-1})$	$k_{R51}(\text{s}^{-1})$
273	$4.3 \times 10^{-18}$	$2.0 \times 10^6$	$2.6 \times 10^6$
280	$5.0 \times 10^{-18}$	$2.9 \times 10^6$	$3.8 \times 10^6$
298	$7.6 \times 10^{-18}$	$7.3 \times 10^6$	$9.5 \times 10^6$
300	$7.9 \times 10^{-18}$	$8.1 \times 10^6$	$1.0 \times 10^7$
320	$1.2 \times 10^{-17}$	$1.9 \times 10^7$	$2.5 \times 10^7$
340	$1.8 \times 10^{-17}$	$4.4 \times 10^7$	$5.6 \times 10^7$
360	$2.6 \times 10^{-17}$	$9.0 \times 10^7$	$1.1 \times 10^8$
380	$3.7 \times 10^{-17}$	$1.7 \times 10^8$	$2.2 \times 10^8$
400	$5.1 \times 10^{-17}$	$3.1 \times 10^8$	$3.8 \times 10^8$

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<sub>2</sub>O radical has two kinds of pathways: (1) it directly decomposes into CH<sub>2</sub>O and OH radical (R40) via β-site C<sub>1</sub>-O<sub>1</sub> bond scission with the barrier of 52.4 kcal·mol<sup>-1</sup>; (2) it converts into HCOOH and HO<sub>2</sub> radical (R41) through H-abstraction by O<sub>2</sub> with the barrier of 26.4 kcal·mol<sup>-1</sup>. This result reveals that R41 is the most feasible channel in the fragmentation of HOCH<sub>2</sub>O radical.*

*The resulting HOCH(CH<sub>3</sub>)O radical has three types of pathways. The first one is β-site C<sub>1</sub>-C<sub>2</sub> bond scission leading to the formation of HCOOH + CH<sub>3</sub>·(R45) with the barrier of 8.3 kcal·mol<sup>-1</sup>. The second one is β-site C<sub>1</sub>-O<sub>1</sub> bond cleavage resulting in formation of CH<sub>3</sub>COH + ·OH (R46) with the barrier of 26.7 kcal·mol<sup>-1</sup>. The third one is H-abstraction by O<sub>2</sub> leading to CH<sub>3</sub>COOH + HO<sub>2</sub>· (R47) with the barrier of 26.2 kcal·mol<sup>-1</sup>. Based on the calculated reaction barriers, it can be found that β-site C<sub>1</sub>-C<sub>2</sub> bond scission is the dominant pathway in the fragmentation of HOCH(CH<sub>3</sub>)O radical.*

*The formed HO(CH<sub>3</sub>)<sub>2</sub>CO radical can either dissociate to CH<sub>3</sub>COOH + CH<sub>3</sub>· (R51) via the C<sub>1</sub>-C<sub>3</sub> bond scission with the barrier of 8.2 kcal·mol<sup>-1</sup>, or decompose into CH<sub>3</sub>COCH<sub>3</sub> + ·OH (R52) through the C<sub>1</sub>-O<sub>1</sub> bond breaking with the barrier of 24.3 kcal·mol<sup>-1</sup>. 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<sub>2</sub>O, HOCH(CH<sub>3</sub>)O and HO(CH<sub>3</sub>)<sub>2</sub>CHO radicals fragmentation are summarized in Table S12. As can be seen in Table S12, *k<sub>R41</sub>* 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<sub>2</sub>] = ~ 5.0 × 10<sup>18</sup> molecule cm<sup>-3</sup>, the pseudo-first-order rate constant *k'<sub>O2</sub>* = *k<sub>R41</sub>*[O<sub>2</sub>] is estimated to be 38.0 s<sup>-1</sup> at room temperature. *k<sub>R45</sub>* vary significantly from 2.0 × 10<sup>6</sup> (273 K) to 3.1 × 10<sup>8</sup> (400 K) s<sup>-1</sup>, and they exhibit a marked positive temperature dependence. Similar phenomenon is also observed from *k<sub>R51</sub>* that *k<sub>R51</sub>* is significantly increased with increasing temperature. *k<sub>R51</sub>* is a factor of ~ 1.3 greater than *k<sub>R45</sub>* 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.*

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

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

- 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 (*ΔG<sub>a</sub><sup>#</sup>* and *ΔE<sub>a</sub><sup>#</sup>*, in italics) for the autoxidation of HOCH<sub>3</sub>CHO radical predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory

**Figure S14.** PES ( $\Delta G_a^\ddagger$  and  $\Delta E_a^\ddagger$ , in italics) for the autoxidation of HO(CH<sub>3</sub>)<sub>2</sub>COO radical predicted at the M06-2X/ma-TZVP//M06-2X/6-311+G(2df,2p) level of theory

- 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

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