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Feb. 9, 2022

Dear Prof. Chan,

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 #3

1. Section 3.2.3 and 3.3: Reviewer 3 raised a valid point about isomerization and molecular size. It is common knowledge in the field that intramolecular rearrangement, such as H-shifts and organic nitrate formation, is important for larger molecules only. It is therefore unsurprising that these detailed quantum chemical calculations show the same. This point should be acknowledged by citing the appropriate literature.

Response: Based on the Reviewer's suggestion, the related references have been cited in the revised manuscript. The isomerization of $HOCH_2OO$ radical proceeds via 1,3-H shifts from the -CH_2 group to the terminal oxygen leading to the formation of hydroperoxyalkyl radical S28. But these isomerization reactions have comparatively high barriers (> 41 kcal mol^{-1}), making them of less importance in the atmosphere. Similar conclusion is also obtained from the isomerization of $HOCH(CH_3)OO$ and $HO(CH_3)_2COO$ radicals that 1,3- and 1,4-H shifts are unfavourable kinetically. The high barriers of 1,3- and 1,4-H shifts can be interpreted as the result of the large ring strain energy (RSE) in the cyclic transition state geometries. As a consequence, the isomerization reactions of $HOCH_2OO$, $HOCH(CH_3)OO$ and $HO(CH_3)_2COO$ radicals are unlikely to proceed in the atmosphere. This conclusion is further supported by the previous studies that the intramolecular H-shift isomerizations are important only for RO_2 radicals with larger carbon structures (Rissanen et al., 2014; Jokinen et al., 2014; Crounse et al., 2013).

The bimolecular reaction of $HOCH_2OO$ radical with NO initially leads to nitrite adduct S31 via the barrierless addition of NO to terminal oxygen atom of $HOCH_2OO$ radical. The formed S31 can either isomerize to organic nitrate S32 via a concerted process of O_2-O_3 bond breaking and O_2-N_1 bond forming with the barrier of 47.8 kcal mol^{-1}, or decompose into $HOCH_2O$ radical and NO_2 via the cleavage of O_2-O_3 bond with the barrier of 11.3 kcal mol^{-1}. The result shows that the latter pathway is more favourable than the former channel. Similar conclusion is also obtained from the reactions of NO with $HOCH(CH_3)OO$ and $HO(CH_3)_2COO$ radicals that the formation of organic nitrate is of minor importance in the atmosphere. This result is further supported by the prior studies that the direct formation of organic nitrate from peroxy nitrites is a minor channel in the reactions of isoprene-derived RO_2 radicals with NO (Piletic et al., 2017; Zhang et al., 2002).

Corresponding descriptions have been revised in the page 24 line 567-571 and page 26 line 614-623 of the revised manuscript:

As a consequence, the isomerization reactions of $HOCH_2OO$*,* $HOCH(CH_3)OO$ *and* $HO(CH_3)_2COO$ *radicals are unlikely to proceed in the atmosphere. This conclusion is further supported by the previous studies that the intramolecular H-shift isomerizations are important only for* RO_2 *radicals with larger carbon structures (Crounse et al., 2013; Jokinen et al., 2014; Rissanen et al., 2014).*

The bimolecular reaction of $HOCH_2OO$ *radical with NO initially leads to nitrite adduct S31 via the barrierless addition of NO to terminal oxygen atom* O_3 *of* $HOCH_2OO$ *radical. S31-cis can either isomerize to organic nitrate S32 (R38) via a concerted process of* O_2*-*O_3 *bond breaking and* O_2*-*N_1 *bond forming with the barrier of 47.8 kcal* mol^{-1}*, or decompose into* $HOCH_2O$ *radical and* NO_2 *(R39) via the cleavage of* O_2*-*O_3 *bond with the barrier of 11.3 kcal* mol^{-1}*. The result shows that the latter pathway is more favourable than the former channel. Similar conclusion is also obtained from the reactions of NO with* $HOCH(CH_3)OO$ *and* $HO(CH_3)_2COO$ *radicals that the formation of organic nitrate is of minor importance in the atmosphere. This result is further supported by the prior studies that the direct formation of organic nitrate from peroxy nitrites is a minor channel in the reactions of isoprene-derived* RO_2 *radicals with NO (Piletic et al., 2017; Zhang et al., 2002).*

2. Section 4: Conclusions should include broader implications, not just summary of results.

Response: Based on the Reviewer's suggestion, the relevant implications have been added in the Conclusion of the revised manuscript.

(a) The dominant pathway is the H-abstraction from the -OOH group in the initiation reactions of OH radical with $HOCH_2OOH$ and $HOC(CH_3)_2OOH$. H-abstraction from the -CH group is competitive with that from the -OOH group in the reaction of OH radical with $HOCH(CH_3)OOH$. The barrier of H-abstraction from the -OOH group is slightly increased as the number of methyl group is increased. Compared with the rate coefficient of dominant pathway in the parent system, it is almost identical when a methyl group substitution occurs at the C_1-position, whereas it reduces by a factor of 2-5 when two methyl groups are introduced into the C_1-position. The atmospheric lifetime of $HOCH_2OOH$, $HOCH(CH_3)OOH$ and $HOC(CH_3)_2OOH$ 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 under the typical OH radical concentrations of 5-15 × 10^6 molecules cm^{-3} during daylight.

(b) The self-reaction of H-abstraction product RO_2 radical initially produces tetroxide intermediate via an oxygen-to-oxygen coupling, then it decomposes into propagation and termination products through the asymmetric two-step O-O bond scission. The rate-limiting step is the first O-O bond cleavage, and the barrier is increased with increasing the number of methyl group. This finding is meaningful to understand the self-reaction of complex RO_2 radicals.

(c) The bimolecular reactions of distinct RO_2 radicals with HO_2 radical lead to the formation of hydroperoxide ROOH as the main product, and the barrier height is independent on the number of methyl substitution. When compared to the rate coefficient for $HOCH_2OO$ + HO_2 reaction, the rate coefficients increase by a factor of 2-5 when one or two methyl groups are introduced into the C1-position. Using a HO_2 radical concentration of ~50 pptv in the forest environments, the pseudo-first-order rate constants k'_{HO2} of distinct RO_2 radical reactions with HO_2 radical vary from 1 to 5 $\times 10^{-2}$ s^{-1}.

(d) The isomerization reactions of $HOCH_2OO$, $HOCH(CH_3)OO$ and $HO(CH_3)_2COO$ radicals are unlikely to proceed in the atmosphere because the intramolecular H-shift steps have dramatically high barriers and strongly endergonic. The result implies that the isomerization of RO_2 radicals with smaller carbon structures is of less importance in the atmosphere.

(e) Reaction with O_2 forming formic acid and HO_2 radical is the dominant removal pathway for $HOCH_2O$ radical formed from the reaction of $HOCH_2OO$ radical with NO. The β-site C-C bond scission is the dominant pathway in the dissociation of $HOCH(CH_3)O$ and $HOC(CH_3)_2O$ radicals formed from the reactions of NO with $HOCH(CH_3)OO$ and $HOC(CH_3)_2OO$ radicals. The result implies that the methyl-substituted alkoxyl radicals primarily proceed via β-site C-C bond scission to produce aldehyde rather than react with O_2.

Corresponding descriptions have been revised in the page 30 line 695-707 and page 31 line 708-732 of the revised manuscript:

(a) The dominant pathway is the H-abstraction from the -OOH group in the initiation reactions of OH radical with $HOCH_2OOH$ and $HOC(CH_3)_2OOH$. H-abstraction from the -CH group is competitive with that from the -OOH group in the reaction of OH radical with $HOCH(CH_3)OOH$. The barrier of H-abstraction from the -OOH group is slightly increased as the number of methyl group is increased. Compared with the rate coefficient of dominant pathway in

the parent system, it is almost identical when a methyl group substitution occurs at the C_1*-position, whereas it reduces by a factor of 2-5 when two methyl groups are introduced into the* C_1*-position. The atmospheric lifetime of* $HOCH_2OOH$*,* $HOCH(CH_3)OOH$ *and* $HOC(CH_3)_2OOH$ *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 under the typical OH radical concentrations of* $5\text{-}15 \times 10^6$ *molecules* cm^{-3} *during daylight.*

(b) The self-reaction of H-abstraction product RO_2 *radical initially produces tetroxide intermediate via an oxygen-to-oxygen coupling, then it decomposes into propagation and termination products through the asymmetric two-step O-O bond scission. The rate-limiting step is the first O-O bond cleavage, and the barrier is increased with increasing the number of methyl group. This finding is meaningful to understand the self-reaction of complex* RO_2 *radicals.*

(c) The bimolecular reactions of distinct RO_2 *radicals with* HO_2 *radical lead to the formation of hydroperoxide ROOH as the main product, and the barrier height is independent on the number of methyl substitution. When compared to the rate coefficient for* $HOCH_2OO + HO_2$ *reaction, the rate coefficients increase by a factor of 2-5 when one or two methyl groups are introduced into the C1-position. Using a* HO_2 *radical concentration of ~50 pptv in the forest environments, the pseudo-first-order rate constants* k'_{HO2} *of distinct* RO_2 *radical reactions with* HO_2 *radical vary from 1 to* 5×10^{-2} s^{-1}*.*

(d) The isomerization reactions of $HOCH_2OO$*,* $HOCH(CH_3)OO$ *and* $HO(CH_3)_2COO$ *radicals are unlikely to proceed in the atmosphere because the intramolecular H-shift steps have dramatically high barriers and strongly endergonic. The result implies that the isomerization of* RO_2 *radicals with smaller carbon structures is of less importance in the atmosphere.*

(e) Reaction with O_2 *forming formic acid and* HO_2 *radical is the dominant removal pathway for* $HOCH_2O$ *radical formed from the reaction of* $HOCH_2OO$ *radical with NO. The* β*-site C-C bond scission is the dominant pathway in the dissociation of* $HOCH(CH_3)O$ *and* $HOC(CH_3)_2O$ *radicals formed from the reactions of NO with* $HOCH(CH_3)OO$ *and* $HOC(CH_3)_2OO$ *radicals. The result implies that the methyl-substituted alkoxyl radicals primarily proceed via* β*-site C-C bond scission to produce aldehyde rather than react with* O_2*.*

3. In general, the manuscript can be understood by a reader, but there are still many language

issues. The manuscript should be reviewed more closely again for clarity. I point out the following issues here, but there are many others I have not pointed out.

Response: Based on the Reviewer's suggestion, the language issues have been corrected carefully in the revised manuscript.

4. Line 32 “is remain” remove “is”.

Response: Based on the Reviewer's suggestion, the word “is” has been removed in the revised manuscript.

Corresponding description has been revised in the page 2 line 27-29 of the revised manuscript:

However, the transformation mechanisms for OH-initiated oxidation of HHPs remain incompletely understood.

5. Line 46 “RO_2 radicals reactions” should be “RO_2 radical reactions”.

Response: Based on the Reviewer's suggestion, the word “RO_2 radicals reactions” has been replaced by “RO_2 radical reactions” in the revised manuscript.

Corresponding description has been revised in the page 2 line 41-43 of the revised manuscript:

The barrier height of distinct RO_2 *radical reactions with* HO_2 *radical is independent on the number of methyl substitution.*

6. Line 49 “dominate” is a verb, not an adjective.

Response: Based on the Reviewer's suggestion, the word “dominate” has been replaced by “dominant” in the revised manuscript.

Corresponding description has been revised in the page 2 line 45-47 of the revised manuscript:

The β*-site C-C bond scission is the dominant pathway in the dissociation of* $HOCH(CH_3)O$ *and* $HOC(CH_3)_2O$ *radicals formed from the reactions of NO with* $HOCH(CH_3)OO$ *and* $HOC(CH_3)_2OO$ *radicals.*

7. Line 51: Dot symbol is used to denote radical species here, but not in other places. Should be consistent.

Response: Based on the Reviewer's suggestion, the dot symbol has been replaced by the word "radical" in the revised manuscript.

8. Line 99: wouldn't HHP come from ozonolysis of all terminal alkenes, not just ethene.

Response: Based on the Reviewer's suggestion, the mentioned sentence has been reworded as "Hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$), the simplest HHPs come from the ozonolysis of all terminal alkenes in the presence of water, is observed in significant abundance in the atmosphere."

Corresponding description has been revised in the page 4 line 92-94 of the revised manuscript:

Hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$*), the simplest HHPs come from the ozonolysis of all terminal alkenes in the presence of water, is observed in significant abundance in the atmosphere (Allen et al., 2018).*

9. Line 100: replace "varies" with "is varied".

Response: Based on the Reviewer's suggestion, the word "varies" has been replaced by "is varied" in the revised manuscript.

Corresponding description has been revised in the page 4 line 94-97 of the revised manuscript:

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).

10. Line 106: awkward phrasing in "A recent experimental study by Allen et al. (2018) conducted ….

Response: Based on the Reviewer's suggestion, the mentioned sentence has been reworded as "Allen et al. conducted the OH-initiated oxidation of HMHP in an environmental chamber and simulated the impact of HMHP oxidation on the global formic acid concentrations using the chemical transport model GEOS-Chem."

Corresponding description has been revised in the page 4 line 100-103 of the revised manuscript:

Allen et al. (2018) conducted the OH-initiated oxidation of HMHP in an environmental chamber and simulated the impact of HMHP oxidation on the global formic acid concentration using the chemical transport model GEOS-Chem.

11. Line 122: "there is few studies" should be "there are few studies"

Response: Based on the Reviewer's suggestion, the sentence "there is few studies" has been replaced by "there are few studies" in the revised manuscript.

Corresponding description has been revised in the page 5 line 116-118 of the revised manuscript:

There are few studies on the subsequent transformations of the resulting H-abstraction products formed from the OH-initiated oxidation of larger HHPs.

12. Line 124 do not start a sentence with "And"

Response: Based on the Reviewer's suggestion, the word "And" has been removed in the revised manuscript.

Corresponding description has been revised in the page 5 line 118-119 of the revised manuscript:

The effect of the size and number of substituents on the rates and outcomes of SOA precursors (e.g. ROOR, HOMs) is uncertain up to now.

13. Line 162 awkward phrasing "is successfully located"

Response: Based on the Reviewer's suggestion, the mentioned sentence has been reworded as "Previous studies have demonstrated that the UDFT method is suitable to identify the minimum of metastable singlet caged radical complex and the transition state of O-O bond homolysis."

Corresponding description has been revised in the page 6 line 154-156 of the revised manuscript:

Previous studies have demonstrated that the UDFT method is suitable to identify the minimum of metastable singlet caged radical complex and the transition state of O-O bond homolysis.

14. Line 196 and thereafter literature is not plural.

Response: Based on the Reviewer’s suggestion, the mentioned sentence has been revised as “Previous literature has demonstrated that the reaction kinetics of multiconformers involvement are more precisely than that of the single conformer approximation”

Corresponding description has been revised in the page 7 line 190-192 of the revised manuscript:

Previous literature has demonstrated that the reaction kinetics of multiconformers involvement are more precisely than that of the single conformer approximation (Møller, et al., 2016, 2020)

15. Line 199 “multiconformers” should be “multiconformer”.

Response: Based on the Reviewer’s suggestion, the word “multiconformers” has been replaced by “multiconformer” in the revised manuscript.

Corresponding description has been revised in the page 7 line 192-193 of the revised manuscript:

Herein, the multiconformer treatment is performed to investigate the H-shift reactions of RO_2 *radicals.*

16. Line 236 “a highly dependent” should be “strong dependence”.

Response: Based on the Reviewer’s suggestion, the word “a highly dependent” has been replaced by “strong dependence” in the revised manuscript.

Corresponding description has been revised in the page 9 line 229-231 of the revised manuscript:

Previous literatures have proposed that the lifetime of CI with respect to the reaction with water vapour exhibits strong dependence on the nature of CIs (Anglada and Solé, 2016; Taatjes, et al., 2013; Anglada, et al., 2011).

17. Line 263 Add “the” to “same conclusion…”.

Response: Based on the Reviewer’s suggestion, the word “the” has been added in the revised manuscript.

Corresponding description has been revised in the page 10 line 257-259 of the revised manuscript:

The same conclusion is also derived from the energy barriers $\Delta E_a^{\#}$ *that R4 is the most favorable H-abstraction pathway.*

18. Line 263 Add “the” to “same conclusion…”.

Response: Based on the Reviewer’s suggestion, the word “the” has been added in the revised manuscript.

Corresponding description has been revised in the page 11 line 291-292 of the revised manuscript:

The same conclusion is also derived from the energy barriers $\Delta E_a^{\#}$ *that the R6' and R8' are the most favourable H-abstraction pathways.*

19. Line 325 Should be “decrease slightly with increasing temperature”.

Response: Based on the Reviewer’s suggestion, the mentioned sentence has been revised as “the total rate coefficients k_{tot} of $HOCH_2OOH$ reaction with OH radical decrease slightly with increasing temperature”.

Corresponding description has been revised in the page 12 line 319-320 of the revised manuscript:

The total rate coefficients k_{tot} *of* $HOCH_2OOH$ *reaction with OH radical decrease slightly with increasing temperature.*

20. Line 337 and in many other instances: replace “are decreased” with “decrease”.

Response: Based on the Reviewer’s suggestion, the word “are decreased” has been replaced by “decrease” in the revised manuscript.

Corresponding descriptions have been revised in the page 12 line 331-334 and page 22 line 517-518 of the revised manuscript:

From Table S3, it can be seen that the total rate coefficients k'_{tot} of $HOCH(CH_3)OOH$ reaction with OH radical decrease in the range of 4.5 × 10^{-11} (273 K) to 8.1 × 10^{-12} (400 K) cm^3 $molecule^{-1}$ s^{-1} with increasing temperature, and they exhibit a slightly negative temperature dependence.

Similar conclusion is also obtained from the rate coefficients k_{R32} and k_{R33} that they decrease with the temperature increasing.

21. Line 345 replace "The reason is most likely due to…" with "The most likely reason is…".

Response: Based on the Reviewer's suggestion, the mentioned sentence has been revised as "The most likely reason is due to the stability of pre-reactive complexes that IM8-a is more stable than IM6-a in energy."

Corresponding description has been revised in the page 13 line 340-341 of the revised manuscript:

The most likely reason is due to the stability of pre-reactive complexes that IM8-a is more stable than IM6-a in energy.

22. Line 356-358 "Compared the barriers…" is an incomplete sentence.

Response: Based on the Reviewer's suggestion, the mentioned sentence has been reworded as "Compared with the barriers of H-abstraction from the -OOH and $-CH_2$ groups in the reaction of OH radical with $HOCH_2OOH$, it can be found that the barrier of H-abstraction from the -CH group is reduced by 3.6 kcal mol^{-1}, whereas the barrier of H-abstraction from the -OOH group is increased by 0.2 kcal mol^{-1} when a methyl group substitution occurs at the C1-position of $HOCH_2OOH$."

Corresponding description has been revised in the page 13 line 351-356 of the revised manuscript:

Compared with the barriers of H-abstraction from the -OOH and $-CH_2$ groups in the reaction of OH radical with $HOCH_2OOH$, it can be found that the barrier of H-abstraction from the -CH group is reduced by 3.6 kcal mol^{-1}, whereas the barrier of H-abstraction from the -OOH group is increased by 0.2 kcal mol^{-1} when a methyl group substitution occurs at the C1-position of $HOCH_2OOH$.

23. Line 370 replace “introduce” with “are introduced”.

Response: Based on the Reviewer’s suggestion, the word “introduce” has been replaced by “are introduced” in the revised manuscript.

Corresponding description has been revised in the page 14 line 362-365 of the revised manuscript:

It can be found that the rate coefficient is almost identical when a methyl group substitution occurs at the C_1*-position, whereas the rate coefficient reduces by a factor of 2-5 when two methyl groups are introduced into the* C_1*-position.*

24. Line 386-387 The wording in “have three types of channels” is a little awkward. I suggest “have three possible fates” or “react via three possible channels”.

Response: Based on the Reviewer’s suggestion, the mentioned sentence has been revised as “In principle, the H-abstraction products RO_2 radicals have three possible fates in pristine environments.”

Corresponding description has been revised in the page 15 line 380-381 of the revised manuscript:

In principle, the H-abstraction products RO_2 *radicals have three possible fates in pristine environments.*

25. Line 398: would it also require RO_2 concentrations to be high.

Response: Based on the Reviewer’s suggestion, the mentioned sentence has been reworded as “The self-reaction is one of dominant removal pathways for RO_2 radicals when the concentration of NO is low and the concentration of RO_2 radicals is high.”

Corresponding description has been revised in the page 16 line 392-393 of the revised manuscript:

The self-reaction is one of dominant removal pathways for RO_2 *radicals when the concentration of NO is low and the concentration of* RO_2 *radicals is high.*

26. Line 453: remove “are” from “are of less importance”.

Response: Based on the Reviewer's suggestion, the word "are" has been removed in the revised manuscript.

Corresponding description has been revised in the page 17 line 446-447 of the revised manuscript:

But the barriers of R20 and R21 are significantly high, making them of less importance in the atmosphere.

27. Line 459-460: awkward phrasing in "accompany with".

Response: Based on the Reviewer's suggestion, the mentioned sentence has been reworded as "These two processes overcome the barriers of 21.4 and 1.3 kcal mol^{-1}, respectively".

Corresponding description has been revised in the page 18 line 453-454 of the revised manuscript:

These two processes overcome the barriers of 21.4 and 1.3 kcal mol^{-1}*, respectively.*

28. Line 460: "it" in "Then it decomposes…" is vague.

Response: Based on the Reviewer's suggestion, the mentioned sentence has been revised as "Then, S21 decomposes into the propagation ($2HOCH(CH_3)O$ + $^3O_2$) and termination products ($HOCH(CH_3)OH$ + $^3CH_3OOH$ + $^3O_2$ and dimer S22 + $^3O_2$) with the exoergicity of 12.5, 11.7 and 33.0 kcal mol^{-1}."

Corresponding description has been revised in the page 18 line 454-456 of the revised manuscript:

Then, S21 decomposes into the propagation ($2HOCH(CH_3)O$ + $^3O_2$) *and termination products* ($HOCH(CH_3)OH$ + $^3CH_3OOH$ + $^3O_2$ *and dimer S22* + $^3O_2$) *with the exoergicity of 12.5, 11.7 and 33.0 kcal* mol^{-1}.

29. Line 472-473: grammatical error in "Different the self-reactions of $HOCH_2OO$ and $HOCH(CH_3)OO$ radicals".

Response: Based on the Reviewer's suggestion, the mentioned sentence has been revised as "Compared with the self-reactions of $HOCH_2OO$ and $HOCH(CH_3)OO$ radicals, it can be found that the termination product of the self-reaction of $HOC(CH_3)_2OO$ radical is exclusively dimer S27."

Corresponding description has been revised in the page 18 line 466-468 of the revised manuscript:

Compared with the self-reactions of $HOCH_2OO$ and $HOCH(CH_3)OO$ radicals, it can be found that the termination product of the self-reaction of $HOC(CH_3)_2OO$ radical is exclusively dimer S27.

30. Line 480: "undergo autoxidation".

Response: Based on the Reviewer's suggestion, the word "undergo autoxidation" has been added in the revised manuscript.

Corresponding description has been revised in the page 18 line 473-475 of the revised manuscript:

It is therefore that the tertiary RO_2 radicals have great opportunity to react with HO_2 radical or undergo autoxidation in pristine environments.

31. Line 480: "pristine environments" or "a pristine environment".

Response: Based on the Reviewer's suggestion, the word "pristine environments" has been used in the revised manuscript.

Corresponding description has been revised in the page 18 line 473-475 of the revised manuscript:

It is therefore that the tertiary RO_2 radicals have great opportunity to react with HO_2 radical or undergo autoxidation in pristine environments.

32. Line 496: awkward phrasing in "The main sources of HO_2 radical involve…".

Response: Based on the Reviewer's suggestion, the mentioned sentence has been reworded as "The primary sources of HO_2 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_2 and the red-light-induced decomposition of α-hydroxy methylperoxy radical $OHCH_2OO$.”

Corresponding description has been revised in the page 21 line 491-497 of the revised manuscript:

The primary sources of HO_2 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_2 and the red-light-induced decomposition of α-hydroxy methylperoxy radical $OHCH_2OO$ (Kumar and Francisco, 2015; Stone et al., 2012; Hofzumahaus et al., 2009).

33. Line 498: typo “senondary”.

Response: Based on the Reviewer’s suggestion, the word “senondary” has been corrected in the revised manuscript.

34. Line 545: awkward phrasing in “resulting finally HOMs…”.

Response: Based on the Reviewer’s suggestion, the mentioned sentence has been reworded as “The autoxidation mechanism includes an intramolecular H-shift from the $-CH_3$ or $-CH_2-$ groups to the -OO site, leading to the formation of a hydroperoxyalkyl radical QOOH, followed by O_2 addition to form a new peroxy radical ($HOOQO_2$), one after the other, resulting in formation of HOMs”

Corresponding description has been revised in the page 21 line 535-539 of the revised manuscript:

The autoxidation mechanism includes an intramolecular H-shift from the $-CH_3$ or $-CH_2-$ groups to the -OO site, leading to the formation of a hydroperoxyalkyl radical QOOH, followed by O_2 addition to form a new peroxy radical ($HOOQO_2$), one after the other, resulting in formation of HOMs (Rissanen et al., 2014; Berndt et al., 2015).

References

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