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Jan. 31, 2019

Dear reviewer,

**Revision for Manuscript acp-2018-935**

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 “**Mechanistic and Kinetics Investigations of Oligomer Formation from Criegee Intermediates Reactions with Hydroxyalkyl Hydroperoxides**”. 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 reviewers 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 sentence on lines 45-48 is plagiarized from Donahue et al.(1) I do not have the resources to fully vet the rest of this manuscript, but all text must be in your own words. You cannot copy such fine sentences as if they were your own. ALL instances of copied text must be removed and replaced with text you produce.

**Response:** We are sorry for this. The original sentence in the revised manuscript is "Alkene ozonolysis produces a carbonyl oxide (also called Criegee intermediates (CIs)) and a carbonyl moiety".

Corresponding descriptions have been revised in the page 3 line 43-46 of the revised manuscript:

*Alkene ozonolysis produces a carbonyl oxide (also called Criegee intermediates (CIs)) and a carbonyl moiety (Donahue et al., 2011; Aplincourt et al., 2000; Johnson et al., 2008; Welz et al., 2012; Criegee et al., 1975; Taatjes et al., 2013).*

Moreover, all text in the revised manuscript has been checked carefully using our own words.

2. Please make clear throughout that the reactions studied are minor loss processes for CI. Your lifetime of 6000 seconds is quite long compared to other CI reactions. In addition, make explicitly clear that you calculate the lifetime with respect to only reaction with HHP. You often speak of just "lifetime" and do not specify reaction with HHP.

**Response:** Previous experimental and theoretical investigations have shown that unimolecular decay of CI and its reaction with water are the dominant chemical sinks (Smith, et al., 2015; Taatjes, et al., 2013; Chao et al., 2015; Anglada, et al., 2016; Long et al., 2016, 2018, Lester et al., 2018). The main products of CIs reactions with water are hydroxyalkyl hydroperoxides (HHPs), which are important sources of hydroperoxides and carbonyl compounds (Anglada, et al., 2016; Kumar, et al., 2014). Although the carbonyl oxides reactions with HHPs are minor loss processes, the type of reactions is very important for understanding the first step of new particle formation from alkenes ozonolysis, particularly in heavily forested area. Our results demonstrate that the oligomer formations from CIs reactions with HHPs are both thermochemically and kinetically favoured.

As shown in Table 2, the room temperature rate coefficient  $k_{R9}$  is  $1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming that the concentration of HO-CH<sub>2</sub>OO-H (Pa<sub>1</sub>) is approximately equal to that of SCIs (~

$5.0 \times 10^4$  molecules  $\text{cm}^{-3}$ , within an order of magnitude uncertainty) in the boreal forest and rural environments of Finland and Germany (Novelli et al., 2016, 2017). The fate  $\tau$  can be written as eqn (1) (Long et al., 2016):

$$\tau = \frac{1}{k[\text{X}]} \quad (1)$$

where  $k$  and  $[\text{X}]$  represent the rate coefficient and the reactant concentration. The atmospheric lifetime of *anti*- $\text{CH}_3\text{CHOO}$  reactivity toward  $\text{Pa}_1$  is  $1.3\text{-}13 \times 10^3$  s. The experimental rate coefficient of *anti*- $\text{CH}_3\text{CHOO}$  reaction with water dimer approximately equals  $\sim 1.0 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  at 298 K (Lin, et al., 2016). The concentration of water dimer is  $5.5 \times 10^{13}$  molecules  $\text{cm}^{-3}$  at 3 km altitude (Long et al., 2016). The atmospheric lifetime of *anti*- $\text{CH}_3\text{CHOO}$  reactivity toward water dimer is  $1.8 \times 10^{-3}$  s. The result implies that the reactions studied are minor loss processes in the atmosphere. However, the  $[(\text{H}_2\text{O})_2]$  decreases significantly with increasing altitudes. For example, at 15 km altitude, the  $[(\text{H}_2\text{O})_2]$  is  $2.7 \times 10^6$  molecules  $\text{cm}^{-3}$  (Long et al., 2016), the atmospheric lifetime of *anti*- $\text{CH}_3\text{CHOO}$  is  $3.4 \times 10^4$  s. As discussed above, it can be found that the *anti*- $\text{CH}_3\text{CHOO} + \text{Pa}_1$  reaction can compete with the *anti*- $\text{CH}_3\text{CHOO} + (\text{H}_2\text{O})_2$  reaction in some regions where the altitude is above 15 km.

Corresponding descriptions have been added in the page 20 line 549-564 of the revised manuscript:

*The room temperature rate coefficient  $k_{R9}$  is  $1.5 \times 10^{-9}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . Assuming that the concentration of  $\text{Pa}_1$  is approximately equal to that of SCIs ( $\sim 5.0 \times 10^4$  molecules  $\text{cm}^{-3}$ , within an order of magnitude uncertainty) in the boreal forest and rural environments of Finland and Germany (Novelli et al., 2016; 2017). The atmospheric lifetime of *anti*- $\text{CH}_3\text{CHOO}$  reactivity toward  $\text{Pa}_1$  can be estimated as  $1.3\text{-}13 \times 10^3$  s. The experimental rate coefficient of reaction R12 approximately equals  $\sim 1.0 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  at 298 K (Lin et al., 2016). The concentration of water dimer is  $5.5 \times 10^{13}$  molecules  $\text{cm}^{-3}$  at 3 km altitude (Long et al., 2016). The atmospheric lifetime of *anti*- $\text{CH}_3\text{CHOO}$  reactivity toward water dimer is  $1.8 \times 10^{-3}$  s. The result implies that the reactions studied are minor loss processes in the atmosphere. However, the  $[(\text{H}_2\text{O})_2]$  decreases significantly with increasing altitudes (Long et al., 2016). For example, at 15 km altitude, the  $[(\text{H}_2\text{O})_2]$  is  $2.7 \times 10^6$  molecules  $\text{cm}^{-3}$ , the atmospheric lifetime of *anti*- $\text{CH}_3\text{CHOO}$  is  $3.4 \times 10^4$  s. As discussed above, it can be found that the *anti*- $\text{CH}_3\text{CHOO} + \text{Pa}_1$  reaction can*

*compete with the anti-CH<sub>3</sub>CHOO + (H<sub>2</sub>O)<sub>2</sub> system in some regions where the altitude is above 15 km.*

3. The products formed may be subject to other loss processes than thermal unimolecular decay, such as photolysis and reaction with more abundant reaction partners (e.g. OH). The authors need to place the chemistry studied here in a broader context and discuss (even if briefly) other loss processes.

**Response:** Based on the Reviewer's suggestion, the bimolecular reaction of HO-CH<sub>2</sub>OO-H(Pa<sub>1</sub>) with OH radical is investigated at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory, and the corresponding potential energy surface is shown in Figure S5. As seen from Figure S5, the hydrogen abstraction reactions between OH and Pa<sub>1</sub> are strongly exothermic and spontaneous, indicating that the occurrence of these reactions in the atmosphere is thermochemically feasible. One can notice that the exothermic reaction RH<sub>γ</sub> releasing energy is significantly higher than that of the RH<sub>α</sub> and RH<sub>β</sub>. The pre-reactive complexes (IM<sub>α</sub>H-a, βH-a, and γH-a) are formed in the entrance channel, and followed by proceed the direct hydrogen abstraction processes leading to the products PH<sub>α</sub>, PH<sub>β</sub>, and PH<sub>γ</sub> plus H<sub>2</sub>O. The free-energy ( $\Delta G_a^\ddagger$ ) barriers predict TSH<sub>α</sub>, TSH<sub>β</sub> and TSH<sub>γ</sub> to lie 6.8, 4.8, and 4.4 kcal mol<sup>-1</sup> above the energies of the corresponding pre-reactive complexes IM<sub>α</sub>H-a, βH-a, and γH-a. The result again shows that the OH abstraction H<sub>γ</sub> atom reaction is the most energetically favorable channel.

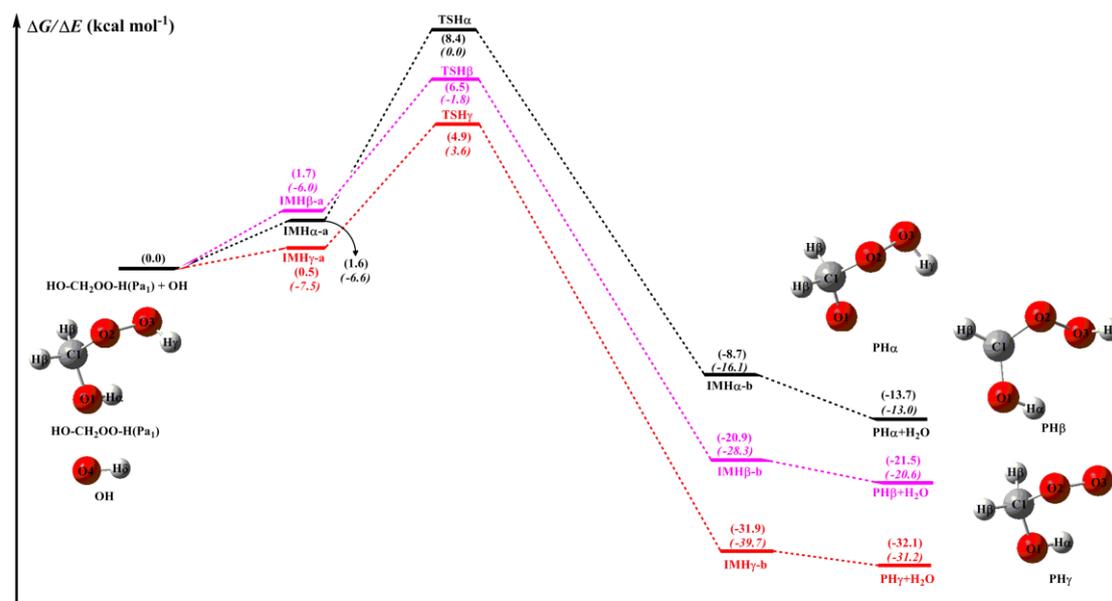
As shown in Figure 2, the addition reactions of 2CH<sub>2</sub>OO + Pa<sub>1</sub> begin with the formation of loosely bound pre-reactive complexes IM1a and IM1b, of 3.1 and 2.6 kcal mol<sup>-1</sup> stability. They are formed by a hydrogen bond between the terminal CH<sub>2</sub>OO oxygen atom and the hydrogen atom of the -OOH group in Pa<sub>1</sub>, and a van der Waals (vdW) bond between the central carbon atom of CH<sub>2</sub>OO and the oxygen atom of the -OH group in Pa<sub>1</sub>. The above complexes are immediately converted into products P1a and P1b via transition states TS1a and TS1b with barriers of 8.4 and 11.7 kcal mol<sup>-1</sup>, respectively, while the corresponding reaction exothermicities are estimated as 43.4 and 40.5 kcal mol<sup>-1</sup>, respectively. The above result shows that the most favorable channel is the addition of the -OOH group of Pa<sub>1</sub> to the parent carbonyl oxide. However, the barrier is higher than that of the corresponding hydrogen abstraction reaction RH<sub>γ</sub> 4.0 kcal mol<sup>-1</sup>, indicating that the photochemical oxidation of hydroxyalkyl hydroperoxides is important in the atmosphere.

In the present study, we mainly focus on the gas phase reaction mechanism and kinetics of

oligomer formation from carbonyl oxides reactions with hydroxyalkyl hydroperoxides. This is because the type of reaction studied is very important for understanding the first step of new particle formation from alkenes ozonolysis, particularly in heavily forested area.

Corresponding descriptions have been added in the page 13 line 339-357 of the revised manuscript:

*Moreover, the bimolecular reaction of  $Pa_1$  with OH radical is investigated at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory, and the corresponding PES is shown in Figure S5. As seen from Figure S5, the hydrogen abstraction reactions between OH and  $Pa_1$  are strongly exothermic and spontaneous, indicating that the occurrence of these reactions in the atmosphere is thermochemically feasible. One can notice that the exothermic reaction  $RH_\gamma$  releasing energy is significantly higher than that of the  $RH_\alpha$  and  $RH_\beta$ . The pre-reactive complexes ( $IMaH-\alpha$ ,  $\beta H-\alpha$ , and  $\gamma H-\alpha$ ) are formed in the entrance channel, and followed by proceed the direct hydrogen abstraction processes leading to the products  $PH_\alpha$ ,  $PH_\beta$ , and  $PH_\gamma$  plus  $H_2O$ . The barriers predict  $TSH_\alpha$ ,  $TSH_\beta$  and  $TSH_\gamma$  to lie 6.8, 4.8, and 4.4 kcal mol<sup>-1</sup> above the energies of the corresponding pre-reactive complexes  $IMaH-\alpha$ ,  $\beta H-\alpha$ , and  $\gamma H-\alpha$ . The result again shows that the reaction  $RH_\gamma$  is the most energetically favorable channel. One can notice that the barrier of  $RH_\gamma$  is lower than that of the corresponding addition reaction  $RIa$  4.0 kcal mol<sup>-1</sup>, indicating that the photochemical oxidation of HHPs is important in the atmosphere. In the present study, we mainly focus on the gas phase reaction mechanism and kinetics of oligomer formation from carbonyl oxides reactions with HHPs. This is because the type of reaction studied is very important for understanding the first step of new particle formation from alkenes ozonolysis, particularly in heavily forested area.*



**Figure S5.** PES ( $\Delta G$  and  $\Delta E$  (italic)) for the reaction of HO-CH<sub>2</sub>OO-H (Pa<sub>1</sub>) with OH computed at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory

4. As the major importance of this work relates to formation of secondary organic aerosol, the authors should make a better attempt to compare the possible influence of this specific chemistry on SOA formation and observed SOA formation from ozonolysis experiments, such as that in Ehn et al.(2) Further it should be clearly stated early on in the manuscript that the reactions studied are gas phase. A reaction with HHP might suggest to many that this chemistry occurs within the particle phase where HHP could have a higher concentration.

**Response:** In the present study, we mainly focus on the gas phase reaction mechanism and kinetics of oligomer formation from carbonyl oxides reactions with HHPs. Our results demonstrate that the consecutive reactions of CIs with HHPs are both thermochemically and kinetically favoured, and the oligomers containing CIs as chain units. Ehn et al. (2014) reported a large source of low-volatility SOA generated from the ozonolysis of  $\alpha$ -pinene and other endocyclic monoterpenes under atmospheric conditions, and proposed that the mechanism of extremely low-volatility organic compounds (ELVOCs) formation is driven by RO<sub>2</sub> autoxidation. The RO<sub>2</sub> autoxidation pathway mainly includes the intramolecular hydrogen shift and the sequential O<sub>2</sub> addition steps (Rissanen, et al., 2014). Compared with the RO<sub>2</sub> autoxidation pathways, oligomerization reactions involving CIs as the repeat units, preserve carbon oxidation state and increase the number of a carbon backbone moiety, and therefore lead to a large reduction in the volatility (Wang, et al., 2016). Moreover, oligomerization reaction proceed over a shorter

period of time during the early stage of biogenic SOA formation and growth (Heaton et al., 2007). Therefore, it is essential to investigate the gas phase Criegee chemistry-based mechanism of SOA formation and growth.

Corresponding descriptions have been added in the page 5 line 116-127 and page 6 line 128-132 of the revised manuscript:

*On the other hand, Ehn et al. (2014) reported a large source of low-volatility SOA generated from the ozonolysis of  $\alpha$ -pinene and other endocyclic monoterpenes under atmospheric conditions, and proposed that the mechanism of extremely low-volatility organic compounds (ELVOCs) formation is driven by  $RO_2$  autoxidation. The  $RO_2$  autoxidation pathway mainly includes the intramolecular hydrogen shift and the sequential  $O_2$  addition steps (Rissanen et al., 2014). Also several groups obtained similar conclusions that the highly oxygenated molecules (HOM) are produced via  $RO_2$  autoxidation in the cyclohexene and terpenes ozonolysis systems (Kirkby et al., 2016; Berndt et al., 2018). Moreover, HOM are major contributors to aerosol particle formation and growth on a global scale (Tröstl et al., 2016; Stolzenburg et al., 2018). Compared with the  $RO_2$  autoxidation pathways, oligomerization reactions involving CIs as the repeat units, preserve carbon oxidation state and increase the number of a carbon backbone moiety, and therefore lead to a large reduction in the volatility (Wang et al., 2016). Moreover, oligomerization reaction proceeds over a shorter period of time during the early stage of biogenic SOA formation and growth (Heaton et al., 2007). Therefore, we think that it is essential to investigate the gas phase Criegee chemistry-based mechanism of SOA formation and growth.*

5. All optimized geometries of the stationary points must be added to supplementary material. Pictures are not sufficient, z-matrices must be included. Also The imaginary frequencies which are used in your Eckart calculations should be included.

**Response:** Based on the Reviewer's suggestion, the optimized geometries, z-matrices and vibrational frequencies of all stationary points are added in the Figures S4, S6-S8, and the imaginary frequencies of all transition states in Eckart calculations are also added in the Figures S4, S6-S8 in the supplementary material.

6. Be very careful about referring to SOAs as individual aerosols. As this work may relate to new particle formation this may technically be correct, but this usage is often problematic. Line 26 has the INCORRECT usage, it should be "secondary organic aerosol (SOA)", because the general

term refers to mass added to existing aerosol due to condensation of material onto existing particles.

**Response:** Based on the Reviewer's suggestion, the secondary organic aerosols (SOA) has been corrected in the revised manuscript.

7. You state the importance of entropy in the free energy barriers, but you do not discuss its origin. Please comment on key vibrational modes that contribute to entropic factors.

**Response:** According to the principle of statistical thermodynamics, the entropy can be described as eqn (2)

$$S = \frac{H - G}{T} \quad (2)$$

where H is the enthalpy, G is the free energy, T is the temperature in Kelvin. The relationship between the entropy and the partition function can be written as eqn (3)

$$S = k \ln \frac{q^N}{N!} + NkT \left( \frac{\partial \ln q}{\partial T} \right)_{V,N} \quad (3)$$

where  $k$  is the Boltzmann constant,  $q$  is the partition function, it mainly includes translation ( $q_{trans}$ ), vibration ( $q_{vib}$ ), external rotation ( $q_{rot}$ ), electronic ( $q_{ele}$ ) and torsional ( $q_{tor}$ ) partition functions ( $q = q_{trans}q_{vib}q_{rot}q_{ele}q_{tor}$ ) (Mendes, et al., 2014). Among these partition functions, the  $q_{vib}$  plays an important role in determining the entropic factors. Thus, the  $q_{vib}$  is used to evaluate the contribution of vibrational mode to the entropic factors. The  $q_{vib}$  is expressed as follows:

$$q_{vib} = \exp\left(-\frac{1}{2} \frac{h\nu}{kT}\right) \times \left(\frac{1}{1 - e^{-h\nu/kT}}\right) \quad (4)$$

Table S2 lists the partition function of every vibrational mode involved in the complex IM1a. As shown in Table S2, the partition functions of low frequency vibrational mode ( $< 200 \text{ cm}^{-1}$ ) are significantly higher than the high frequency vibrational mode ( $> 200 \text{ cm}^{-1}$ ), and their contribution is up to 70.5 percent. The result implies that the low frequency vibrational mode contributes to entropic factor is significant. Similar conclusion is also obtained from the IM2a case (Table S3).

Corresponding descriptions have been added in the page 11 line 293-299 of the revised manuscript:

*The partition function of every vibrational mode involved in the complex IM1a is listed in Table S2. As shown in Table S2, the partition function of low frequency vibrational mode ( $< 200$*

$\text{cm}^{-1}$ ) is significantly higher than the high frequency vibrational mode ( $> 200 \text{ cm}^{-1}$ ), and their contribution is up to 70.5 percent. The result implies that the low frequency vibrational mode contributes to entropic factor is significant. Similar conclusion is also obtained from the IM2a case (Table S3).

**Table S2** The partition function of every vibrational mode involved in the complex IM1a

<i>N</i>	<i>v</i>	$q_{\text{vib}}$	percent(%)
1	51.49	4.03	30.43
2	123.66	1.66	12.52
3	149.16	1.37	10.31
4	158.76	1.28	9.66
5	199.39	1.00	7.58
6	242.53	0.81	6.12
7	257.19	0.76	5.74
8	422.78	0.42	3.15
9	501.75	0.33	2.48
10	538.04	0.30	2.24
11	642.00	0.22	1.69
12	723.92	0.18	1.37
13	858.58	0.13	0.97
14	896.89	0.12	0.89
15	958.09	0.10	0.76
16	1070.70	0.08	0.58
17	1093.27	0.07	0.55
18	1112.93	0.07	0.52
19	1134.12	0.07	0.50
20	1270.31	0.05	0.36
21	1300.08	0.04	0.33
22	1397.45	0.03	0.26
23	1429.61	0.03	0.24
24	1456.77	0.03	0.23
25	1506.87	0.03	0.20
26	1588.46	0.02	0.17
27	1674.72	0.02	0.13
28	3088.99	0.00	0.00
29	3148.98	0.00	0.00
30	3162.08	0.00	0.00
31	3162.65	0.00	0.00
32	3305.08	0.00	0.00
33	3868.49	0.00	0.00

**Table S3** The partition function of every vibrational mode involved in the complex IM2a

<i>N</i>	<i>v</i>	$q_{\text{vib}}$	percent(%)
1	45.57	4.56	19.74
2	66.77	3.10	13.44
3	93.88	2.20	9.52
4	102.82	2.00	8.68
5	122.46	1.67	7.25
6	144.25	1.41	6.12
7	151.51	1.34	5.82
8	186.88	1.08	4.66

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9	236.15	0.84	3.62
10	242.41	0.81	3.52
11	324.58	0.58	2.51
12	383.38	0.47	2.05
13	460.65	0.37	1.61
14	475.56	0.35	1.54
15	546.86	0.29	1.25
16	589.00	0.26	1.12
17	676.46	0.20	0.89
18	704.48	0.19	0.82
19	751.93	0.17	0.73
20	889.93	0.12	0.52
21	904.59	0.12	0.50
22	957.33	0.10	0.44
23	1053.66	0.08	0.35
24	1082.87	0.07	0.33
25	1103.67	0.07	0.31
26	1123.39	0.07	0.29
27	1129.87	0.07	0.29
28	1139.95	0.06	0.28
29	1188.07	0.06	0.25
30	1271.30	0.05	0.20
31	1306.97	0.04	0.19
32	1353.81	0.04	0.17
33	1383.99	0.04	0.16
34	1415.10	0.03	0.14
35	1438.67	0.03	0.14
36	1455.62	0.03	0.13
37	1457.70	0.03	0.13
38	1501.08	0.03	0.12
39	1569.37	0.02	0.10
40	1663.59	0.02	0.08
41	3104.57	0.00	0.00
42	3113.88	0.00	0.00
43	3140.47	0.00	0.00
44	3173.49	0.00	0.00
45	3187.95	0.00	0.00
46	3286.9	0.00	0.00
47	3436.06	0.00	0.00
48	3910.66	0.00	0.00

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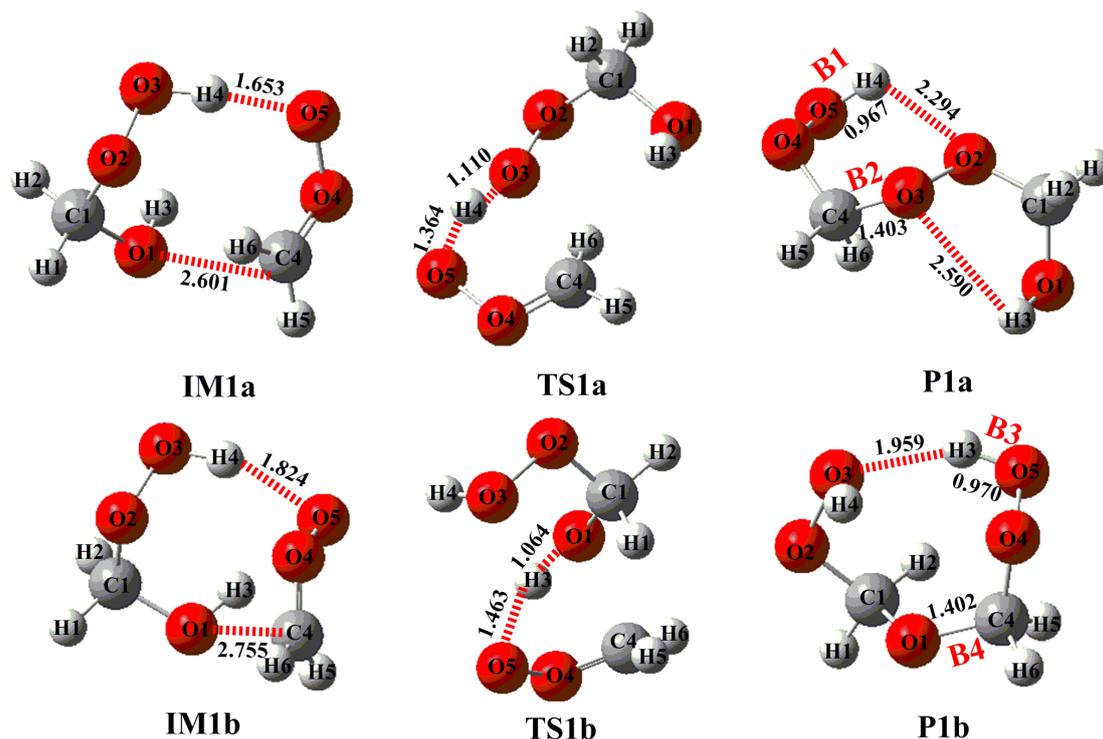
8. Did the authors look for cyclic products? For example products where both dashed bonds in IM1a becoming full covalent bonds?

**Response:** All the pre-reactive complexes and products involved in the title reaction system

are the cyclic structures. For example, the bimolecular reaction of CH<sub>2</sub>OO with HO-CH<sub>2</sub>OO-H (Pa<sub>1</sub>) begins with the barrierless formation of pre-reactive complexes IM1a and IM1b held together by weak hydrogen bonds and vdW forces. Then, the -OOH and -OH fragments in Pa<sub>1</sub> immediately add to the CH<sub>2</sub>OO central carbon atom to produce P1a and P1b. The detailed reaction mechanism mainly includes that the -O3(-O1) fragment of Pa<sub>1</sub> moves to approach the CH<sub>2</sub>OO central carbon atom, whereas the -H4(-H3) atom gets attached to the terminal oxygen atom leading to products P1a and P1b (see Table S4). In the revised manuscript, atoms in molecules (AIM) analysis at the bond critical point (BCP) for the forming bonds (B1(O5-H4), B2(O3-C4), B3(O5-H3) and B1(O1-C4)) is performed with M06-2X functional (Biegler et al., 2000). The electronic density ( $\rho$ ), Laplacian ( $\nabla^2$ ), and the three eigenvalues of the Hessian of BCP are listed in Table S4. As shown in Table S4, the  $\nabla^2$  values of all forming bonds are negative, indicating that they are covalent bonds. The  $\rho$  values of B1 and B3 are significantly higher than that of the B2 and B4, showing that the bond strength of the former case is higher than the latter case.

Corresponding descriptions have been added in the page 12 line 320-326 of the revised manuscript:

*The electronic density ( $\rho$ ), Laplacian ( $\nabla^2$ ), and the three eigenvalues of the Hessian of the complexes IM1a and IM1b are displayed in Table S4. As shown in Table S4, the  $\nabla^2$  values of all forming bonds (B1(O5-H4), B2(O3-C4), B3(O5-H3) and B1(O1-C4)) are negative, indicating that they are covalent bonds. The  $\rho$  values of B1 and B3 are significantly higher than that of the B2 and B4, showing that the bond strength of the former case is higher than the latter case.*



**Table S4** AIM properties at the bond critical points for the forming bonds B1-B4

Bond	$\rho$ ( $e/\text{\AA}^3$ )	$\nabla^2$ ( $e/\text{\AA}^3$ )	Eigenvalue 1	Eigenvalue 2	Eigenvalue 3
B1(O5-H4)	0.370	-2.776	-1.9316	-1.8598	1.0148
B2(O3-C4)	0.271	-0.559	-0.5734	-0.5112	0.5258
B3(O5-H3)	0.364	-2.760	-1.945	-1.8743	1.0588
B4(O1-C4)	0.269	-0.565	-0.5734	-0.5054	0.5139

9. Do you rely solely on free energy estimate outputs? Are other methods such as SCTST too costly?

**Response:** The rate coefficients of elementary reactions are calculated using a combination of canonical transition state theory (CTST) and an asymmetric Eckart tunneling correction based on the free energies obtained from the M06-2X method, in the temperature range from 273 to 400 K. The predicted free energies are equal to the thermal correction to Gibbs free energies at the M06-2X/6-311+G(2df,2p) level plus the electronic energies obtained at the M06-2X/def2-TZVP level. In order to assess the reliability of our kinetics study, the rate coefficients of HO-CH<sub>2</sub>OO-H (Pa<sub>1</sub>) + CH<sub>2</sub>OO (R1a) and HO-CH<sub>2</sub>OO-H (Pa<sub>1</sub>) + *anti*-CH<sub>3</sub>CHOO (R9) reactions are recomputed employing the canonical variational transition state theory (CVTST) with Eckart tunneling correction. The calculated result is listed in Table S9. As shown in Table S9, the predicted rate

coefficients  $k_{CTST(R1a)}$  and  $k_{CVTST(R1a)}$  decrease with increasing temperature, and they exhibit a negative temperature dependence. The difference between  $k_{CTST(R1a)}$  and  $k_{CVTST(R1a)}$  decreases in the range of 2.3 (273 K) to 1.8 (400 K). Such discrepancy between CTST and CVTST ones is acceptable. Similar conclusion is also obtained from the rate coefficients between  $k_{CTST(R9)}$  and  $k_{CVTST(R9)}$ . It is concluded that the CTST/Eckart method allows one to reliably describe the kinetics parameters.

Corresponding descriptions have been added in the page 18 line 506 and page 19 line 507-514 of the revised manuscript:

*In order to assess the reliability of our kinetics study, the rate coefficients of some selected reactions R1a and R9 are recomputed employing the canonical variational transition state theory (CVTST) with Eckart tunneling correction. The calculated result is listed in Table S9. As shown in Table S9, the difference between  $k_{CTST(R1a)}$  and  $k_{CVTST(R1a)}$  decreases in the range of 2.3 (273 K) to 1.8 (400 K). Such rate coefficients discrepancy between CTST and CVTST ones is acceptable. Similar conclusion is also obtained from the rate coefficients between  $k_{CTST(R9)}$  and  $k_{CVTST(R9)}$ . It is concluded that the CTST/Eckart method allows one to reliably describe the kinetics parameters.*

**Table S9** Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of elementary reactions R1a and R9 computed

$T$	$k_{CTST(R1a)}$	$k_{CVTST(R1a)}$	$k_{CTST(R9)}$	$k_{CVTST(R9)}$
273	$1.2 \times 10^{-11}$	$3.5 \times 10^{-11}$	$5.5 \times 10^{-9}$	$1.3 \times 10^{-8}$
280	$9.4 \times 10^{-12}$	$2.6 \times 10^{-11}$	$3.7 \times 10^{-9}$	$8.5 \times 10^{-9}$
298	$5.4 \times 10^{-12}$	$1.4 \times 10^{-11}$	$1.5 \times 10^{-9}$	$3.2 \times 10^{-9}$
300	$5.1 \times 10^{-12}$	$1.3 \times 10^{-11}$	$1.3 \times 10^{-9}$	$2.9 \times 10^{-9}$
320	$3.0 \times 10^{-12}$	$7.2 \times 10^{-12}$	$5.5 \times 10^{-10}$	$1.1 \times 10^{-9}$
340	$1.9 \times 10^{-12}$	$4.2 \times 10^{-12}$	$2.6 \times 10^{-10}$	$5.0 \times 10^{-10}$
360	$1.2 \times 10^{-12}$	$2.7 \times 10^{-12}$	$1.4 \times 10^{-10}$	$2.4 \times 10^{-10}$
380	$8.6 \times 10^{-13}$	$1.8 \times 10^{-12}$	$7.1 \times 10^{-11}$	$1.3 \times 10^{-10}$
400	$6.3 \times 10^{-13}$	$1.2 \times 10^{-12}$	$4.1 \times 10^{-11}$	$7.3 \times 10^{-11}$

10. In sections 3.3 and 3.4, the discussion of loss processes for CI is flawed. Unimolecular decay is always a significant loss process. You seem to misinterpret the references you cite, both Drozd et al. and Long et al. find short thermal lifetimes for the CI formed in ozonolysis.(3,4) The

authors must revise their statements to make clear that CI generally have significant unimolecular decay.

**Response:** Long et al. (2016) proposed that the predominant pathway of unimolecular decay of *syn*-CH<sub>3</sub>CHOO is isomerization to vinyl hydroperoxide (VHP) via the hydrogen atom migration from the methyl group to the terminal oxygen atom, then the decomposition of VHP produces OH radical. Also Donahue et al. (2011) obtained similar conclusion that *syn*-CI isomerization to VHP is preferable due to the low ring strain of H-atom transfer transition state. Both the prompt and thermal unimolecular decay of the energized VHP may dissociate to OH radical, and their yields are strongly pressure and temperature dependents (Kroll, et al., 2001a,b). The preferable route of unimolecular decay of *anti*-CH<sub>3</sub>CHOO is ring-closure to dioxirane via an oxygen atom transfer (Donahue et al, 2011; Taatjes et al., 2013; Long et al., 2016). The dioxirane can finally isomerize to acetic acid via the “hot acid” channel (Kroll, et al., 2001a). Alternatively, the *syn*- and *anti*-CH<sub>3</sub>CHOO may undergo bimolecular reactions with water vapor lead to the formation of HO-C(CH<sub>3</sub>)HOO-H (Anglada et al., 2011).

Long et al. (2018) proposed that the unimolecular decay of (CH<sub>3</sub>)<sub>2</sub>COO is the predominant pathway above 240 K, whereas it can compete with the reaction (CH<sub>3</sub>)<sub>2</sub>COO + SO<sub>2</sub> below 240 K. Drozd et al. (2017) elucidated that tunneling for both the thermal and prompt unimolecular decay of (CH<sub>3</sub>)<sub>2</sub>COO is significant. Also Lester et al. (2018) obtained similar conclusion in the unimolecular decay of (CH<sub>3</sub>)<sub>2</sub>COO to OH radical reaction that the contribution of tunneling to the unimolecular decay rates is significant. Alternatively, the (CH<sub>3</sub>)<sub>2</sub>COO may react with water vapour leading to the formation of HO-C(CH<sub>3</sub>)<sub>2</sub>OO-H (Anglada et al., 2016).

Corresponding descriptions have been added in the page 14 line 380-389, page 15 line 390-393 and page 16 line 437-445 of the revised manuscript:

*Long et al. (2016) proposed that the predominant pathway of unimolecular decay of syn-CH<sub>3</sub>CHOO is isomerization to vinyl hydroperoxide (VHP) via the hydrogen atom migration from the methyl group to the terminal oxygen atom, then the decomposition of VHP produces OH radical. Also Donahue et al. (2011) obtained similar conclusion that syn-CI isomerization to VHP is preferable due to the low ring strain of H-atom transfer transition state. Both of the prompt and thermal unimolecular decay of the energized VHP may dissociate to OH radical, and their yields are strongly pressure and temperature dependents (Kroll et al., 2001a,b). The preferable route of*

*unimolecular decay of anti-CH<sub>3</sub>CHOO is ring-closure to dioxirane via an oxygen atom transfer (Donahue et al., 2011; Taatjes et al., 2013; Long et al., 2016). The dioxirane can finally isomerize to acetic acid via the “hot acid” channel (Kroll et al., 2011b). Alternatively, the syn- and anti-CH<sub>3</sub>CHOO may undergo bimolecular reactions with water vapor lead to the formation of HO-C(CH<sub>3</sub>)HOO-H (Anglada et al., 2011).*

*Long et al. (2018) proposed that the unimolecular decay of (CH<sub>3</sub>)<sub>2</sub>COO is the predominant pathway above 240 K, whereas it can compete with the reaction (CH<sub>3</sub>)<sub>2</sub>COO + SO<sub>2</sub> below 240 K. Drozd et al. (2017) elucidated that tunneling for both the thermal and prompt unimolecular decay of (CH<sub>3</sub>)<sub>2</sub>COO is significant. Also Lester et al. (2018) obtained similar conclusion in the unimolecular decay of (CH<sub>3</sub>)<sub>2</sub>COO to OH radical reaction that the contribution of tunneling to the unimolecular decay rates is significant. Alternatively, the (CH<sub>3</sub>)<sub>2</sub>COO may react with water vapour leading to the formation of HO-C(CH<sub>3</sub>)<sub>2</sub>OO-H (Anglada et al., 2016).*

11. The energy labels in the supplement are confusing. The italics/non-italics energies are not always in same vertical order. Change the figure labels to make the non-italics energy the upper number in all cases. Do this for the main manuscript figures as well.

**Response:** Based on the Reviewer’s suggestion, the non-italics energies have been placed in the upper number in the manuscript and supplement figures.

12. There are a number of awkward sentences/phrases, missing words, or grammatically confusing sentences. Carefully check over this document. I have listed a number of these below.

Line 27 change to “influence”

Line 43 Add Guenther et al as a reference for alkene emissions.5

Line 119 change to “is the dominant..”

132 change to “reactions occur during the...”

147 change to “there is little known of the reactivity...”

167 change to “represents”

168 change to “needs”

238 change to “possess OH and OOH”

246 change to “particularly”

267 - It is confusing to see a negative energy of stability, re-word this, and other instances, to be clearer.

315-317 You have an error the citations to Kroll et al. The year should be 2001.(6,7)

**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.

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