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Reply on RC1

Long Chen et al.

Author comment on "Oligomer formation from the gas-phase reactions of Criegee intermediates with hydroperoxide esters: mechanism and kinetics" by Long Chen et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-376-AC1, 2022

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Dear Prof. Kourtchev,

Revision for Manuscript ACP-2022-376

We thank you very much for giving us the opportunity to revise our manuscript. We highly appreciate the reviewers for their comments and suggestions on the manuscript entitled “**Oligomer formation from the gas-phase reactions of Criegee intermediates with hydroperoxide esters: mechanism and kinetics**”. We have made revisions of our manuscript carefully according to the comments and suggestions of reviewers. 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

- The authors should explain their variational TST calculations for barrierless reactions (p.7) in more detail, particularly since they consistently predict higher CI + HCOOH rate constants than experiment (p.10-11).

Response: In the original manuscript, the rate coefficients for the barrierless reactions are calculated by employing the variational transition state theory (VTST), and the rate coefficients for the bimolecular reactions with the tight transition states are computed by using the canonical transition state theory (CTST) along with one-dimensional asymmetric Eckart tunneling correction. For the initiation reactions of distinct stabilized Criegee intermediates (SCIs) with HCOOH, there are four possible pathways, namely (1) 1,4 O-H insertion (Entry 1), (2) 1,2 O-H insertion (Entry 2), (3) C-H insertion (Entry 3), and (4) C=O cycloaddition (Entry 4), in which Entry 1 is barrierless and Entry 2-4 have the tight transition states. The total rate coefficient for the reaction of SCIs with HCOOH is equal to the sum of the rate coefficient of each pathway. For the barrierless 1,4 O-H insertion reaction, the VTST is approximated with a Morse potential function, $V(\mathrm{R}) = D_e \{1-\exp[-\beta(R-R_e)]\}^2$, along with an anisotropy potential function to stand for the minimum energy path, which is used to calculate the rate coefficients (Raghunath et al., 2017). Here, D_e is the bond energy excluding the zero-point energy, R is the reaction coordinate, and R_e is the equilibrium value of R. It is assumed that the stretching potential in an anisotropy potential is used in conjunction with a potential form of $V_{\mathrm{anisotropy}} = V_0[1-\cos^2(\theta_1-\theta_{1e}) \times \cos^2(\theta_2-\theta_{2e})]$ (Raghunath et al., 2017). Here, V_0 is the stretching potential, which stands for by a Morse potential, θ_1 and θ_{1e} represent the rotational angle between fragment 1 and the reference axis and the equilibrium bond angle of fragment 1, θ_2 and θ_{2e} stand for the rotational angle between fragment 2 and the reference axis and the equilibrium bond angle of fragment 2. The association curve for the reaction of 1,4 O-H insertion of SCIs into HCOOH is computed at the M06-2X/6-311+G(2df,2p) level of theory to cover a range from 0.97 to 1.97 Å at step size 0.1 Å for O-H bond and from 1.44 to 2.44 Å at step size 0.1 Å for C-O bond, while other structural parameters are fully optimized. The computed potential energies are fitted to the Morse potential function. However, the calculated rate coefficients for the reactions of SCIs with HCOOH are higher than the prior experimental measurements. The reason is ascribed to the fact that the approximation of VTST using a Morse potential function in conjunction with an anisotropy potential function is unsuitable to predict the rate coefficients for the barrierless 1,4 O-H insertion reaction.

In the revised manuscript, the rate coefficients for the barrierless reactions are computed by employing the inverse Laplace transformation (ILT) method, and the rate coefficients for the bimolecular reactions with the tight transition states are calculated by utilizing CTST in conjunction with Eckart tunneling correction. The ILT and CTST/Eckart calculations are performed by using the MESMER 6.0 and KiSThelP 2019 programs, respectively (Glowacki et al., 2012; Canneaux et al., 2013). In the ILT treatment, the rotational constants, vibrational frequencies, molecular weights, energies and other input parameters are obtained from the M06-2X/6-311+G(2df,2p) or M06-2X/ma-TZVP methods. For the barrierless reaction of 1,4 O-H insertion of SCIs into HCOOH, SCIs and HCOOH are assigned as the deficient and excess reactants, respectively. The concentration of HCOOH is given a value of 5.0×10^{10} molecules cm^{-3} in the simulation, which is taken from the typical concentration of HCOOH in the tropical forest environments (Vereecken, 2012). N_2 is applied as the buffer gas. A single exponential down model is employed to simulate the collision transfer ($\langle \Delta E \rangle_{\mathrm{down}} = 200\ \mathrm{cm}^{-1}$). The collisional Lennard-Jones parameters are estimated with the empirical formula described by Gilbert and Smith (1990).

The rate coefficients of each elementary pathway included in the initiation reactions of distinct SCIs with HCOOH are calculated in the temperature range of 273-400 K, as listed in Table S3-S6. As shown in Table S3, the total rate coefficients $k_{\text{tot-CH2OO}}$ of CH_2OO reaction with HCOOH are in excess of 1.0×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, and they exhibit a slightly negative temperature dependence in the temperature range studied. $k_{\text{tot-CH2OO}}$ is estimated to be 1.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298 K, which is in good agreement with the experimental values reported by Welz et al. (2014) ($[1.1 \pm 0.1] \times 10^{-10}$), Chung et al. (2019) ($[1.4 \pm 0.3] \times 10^{-10}$), and Peltola et al. (2020) ($[1.0 \pm 0.03] \times 10^{-10}$). $k(TS_{\text{ent1}})$ is approximately equal to $k_{\text{tot-CH2OO}}$ in the whole temperature range, and it decreases in the range of 1.7×10^{-10} (273 K) to 1.2×10^{-10} (400 K) cm^3 $molecule^{-1}$ s^{-1} with increasing temperature. $k(TS_{\text{ent1}})$ is several orders of magnitude greater than $k(TS_{\text{ent2}})$, $k(TS_{\text{ent3}})$ and $k(TS_{\text{ent4}})$ over the temperature range from 273 to 400 K. The result again shows that the barrierless 1,4 O-H insertion reaction is predominant. Similar conclusion is also obtained from the results of the rate coefficients for the reactions of HCOOH with *anti*-CH_3CHOO, *syn*-CH_3CHOO and $(CH_3)_2COO$ (Table S4-S6). At ambient temperature, the total rate coefficients of HCOOH reactions with *anti*-CH_3CHOO, *syn*-CH_3CHOO and $(CH_3)_2COO$ are estimated to be 5.9, 2.7 and 4.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively, which are consistent with the prior experimental measurements of 5 ± 3, 2.5 ± 0.3 and 4.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Welz et al., 2014; Chung et al., 2019; Sipilä et al., 2014).

Table S3 Rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) of each elementary pathway involved in the initiation reaction of CH_2OO with HCOOH computed at different temperatures

T/K	k (TS_{ent1})	k (TS_{ent2})	k (TS_{ent3})	k (TS_{ent4})	$k_{\text{tot-CH2OO}}$
273	1.7×10^{-10}	3.6×10^{-12}	1.0×10^{-22}	3.6×10^{-12}	1.8×10^{-10}
280	1.6×10^{-10}	2.9×10^{-12}	1.2×10^{-22}	3.1×10^{-12}	1.7×10^{-10}
298	1.4×10^{-10}	1.9×10^{-12}	2.2×10^{-22}	2.3×10^{-12}	1.4×10^{-10}
300	1.4×10^{-10}	1.8×10^{-12}	2.4×10^{-22}	2.2×10^{-12}	1.4×10^{-10}
320	1.3×10^{-10}	1.2×10^{-12}	4.9×10^{-22}	1.6×10^{-12}	1.3×10^{-10}

340	1.3×10^{-10}	8.2×10^{-13}	1.0×10^{-21}	1.3×10^{-12}	1.3×10^{-10}
360	1.2×10^{-10}	5.9×10^{-13}	2.2×10^{-21}	1.0×10^{-12}	1.2×10^{-10}
380	1.2×10^{-10}	4.5×10^{-13}	4.5×10^{-21}	8.2×10^{-13}	1.2×10^{-10}
400	1.2×10^{-10}	3.5×10^{-13}	9.0×10^{-21}	6.9×10^{-13}	1.2×10^{-10}

Table S4 Rate coefficients (cm^3 molecule^{-1} s^{-1}) of each elementary pathway involved in the initiation reaction of *anti*-CH_3CHOO with HCOOH computed at different temperatures

T/K	k (TS$_{ent1}$-*anti*)	k (TS$_{ent2}$-*anti*)	k (TS$_{ent3}$-*anti*)	k (TS$_{ent4}$-*anti*)	$k_{tot\text{-}anti}$
273	5.9×10^{-10}	4.2×10^{-11}	5.5×10^{-22}	6.1×10^{-11}	6.9×10^{-10}
280	5.7×10^{-10}	3.8×10^{-11}	6.7×10^{-22}	4.9×10^{-11}	6.6×10^{-10}
298	5.4×10^{-10}	2.3×10^{-11}	1.2×10^{-21}	3.0×10^{-11}	5.9×10^{-10}
300	5.3×10^{-10}	2.0×10^{-11}	1.3×10^{-21}	2.8×10^{-11}	5.8×10^{-10}
320	5.0×10^{-10}	1.5×10^{-11}	2.6×10^{-21}	1.7×10^{-11}	5.3×10^{-10}

340	4.7×10^{-10}	9.4×10^{-12}	5.4×10^{-21}	1.1×10^{-11}	4.9×10^{-10}
360	4.5×10^{-10}	7.0×10^{-12}	1.1×10^{-20}	7.8×10^{-12}	4.7×10^{-10}
380	4.4×10^{-10}	3.6×10^{-12}	2.1×10^{-20}	5.6×10^{-12}	4.5×10^{-10}
400	4.3×10^{-10}	2.0×10^{-12}	4.0×10^{-20}	4.2×10^{-12}	4.4×10^{-10}

Table S5 Rate coefficients (cm^3 molecule^{-1} s^{-1}) of each elementary pathway involved in the initiation reaction of *syn*-CH_3CHOO with HCOOH computed at different temperatures

T/K	k (TS$_{\mathrm{ent1}}$-*syn*)	k (TS$_{\mathrm{ent2}}$-*syn*)	k (TS$_{\mathrm{ent3}}$-*syn*)	k (TS$_{\mathrm{ent4}}$-*syn*)	$k_{\text{tot-}syn}$
273	3.1×10^{-10}	9.5×10^{-13}	4.6×10^{-27}	7.5×10^{-16}	3.1×10^{-10}
280	2.8×10^{-10}	8.0×10^{-13}	7.1×10^{-27}	6.4×10^{-16}	2.8×10^{-10}
298	2.7×10^{-10}	5.4×10^{-13}	8.9×10^{-26}	5.5×10^{-16}	2.7×10^{-10}
300	2.7×10^{-10}	5.2×10^{-13}	9.9×10^{-26}	4.6×10^{-16}	2.7×10^{-10}
320	2.5×10^{-10}	3.6×10^{-13}	3.0×10^{-25}	3.8×10^{-16}	2.5×10^{-10}

340	2.5×10^{-10}	2.6×10^{-13}	9.1×10^{-25}	3.1×10^{-16}	2.5×10^{-10}
360	2.3×10^{-10}	2.0×10^{-13}	2.6×10^{-24}	3.0×10^{-16}	2.3×10^{-10}
380	2.2×10^{-10}	1.5×10^{-13}	7.2×10^{-24}	2.4×10^{-16}	2.2×10^{-10}
400	2.2×10^{-10}	1.2×10^{-13}	1.8×10^{-23}	2.2×10^{-16}	2.2×10^{-10}

Table S6 Rate coefficients (cm^3 molecule^{-1} s^{-1}) of each elementary pathway involved in the initiation reaction of $(CH_3)_2OO$ with HCOOH computed at different temperatures

T/K	k (TS$_{\text{ent1}}$-dim)	k (TS$_{\text{ent2}}$-dim)	k (TS$_{\text{ent3}}$-dim)	k (TS$_{\text{ent4}}$-dim)	$k_{\text{tot-}dim}$
273	5.3×10^{-10}	6.8×10^{-12}	1.4×10^{-26}	4.4×10^{-15}	5.4×10^{-10}
280	5.1×10^{-10}	5.2×10^{-12}	2.2×10^{-26}	4.2×10^{-15}	5.2×10^{-10}
298	4.8×10^{-10}	2.8×10^{-12}	8.0×10^{-26}	4.0×10^{-15}	4.8×10^{-10}
300	4.7×10^{-10}	2.6×10^{-12}	9.2×10^{-26}	3.9×10^{-15}	4.7×10^{-10}
320	4.5×10^{-10}	1.4×10^{-12}	3.6×10^{-25}	3.7×10^{-15}	4.5×10^{-10}

340	4.2×10^{-10}	8.6×10^{-13}	1.3×10^{-24}	3.6×10^{-15}	4.2×10^{-10}
360	3.9×10^{-10}	5.5×10^{-13}	4.5×10^{-24}	3.5×10^{-15}	3.9×10^{-10}
380	3.7×10^{-10}	3.7×10^{-13}	1.4×10^{-23}	3.4×10^{-15}	3.7×10^{-10}
400	3.7×10^{-10}	2.6×10^{-13}	3.9×10^{-23}	3.4×10^{-15}	3.7×10^{-10}

Corresponding descriptions have been added in the page 7 line 173-190, page 11 line 303-315, page 12 line 330-338 and page 13 line 346-351 of the revised manuscript:

The rate coefficients for the barrierless reactions are determined by employing the inverse Laplace transformation (ILT) method. The ILT calculations are performed with the MESMER 6.0 program (Glowacki et al., 2012). In the ILT treatment, the rotational constants, vibrational frequencies, molecular weights, energies and other input parameters are obtained from the M06-2X/6-311+G(2df,2p) or M06-2X/ma-TZVP methods. For the barrierless reaction of 1,4 O-H insertion of SCIs into HCOOH, SCIs and HCOOH are assigned as the deficient and excess reactants, respectively. The concentration of HCOOH is given a value of 5.0×10^{10} *molecules cm*$^{-3}$ *in the simulation, which is taken from the typical concentration of HCOOH in the tropical forest environments (Vereecken et al., 2012).* N_2 *is applied as the buffer gas. A single exponential down model is employed to simulate the collision transfer (*$\langle \Delta E \rangle_{down} = 200$ cm^{-1}*). The collisional Lennard-Jones parameters are estimated with the empirical formula described by Gilbert and Smith (1990).*

The rate coefficients for the bimolecular reactions with the tight transition states are calculated by using the canonical transition state theory (CTST) along with one-dimensional asymmetric Eckart tunneling correction (Truhlar et al., 1996; Eckart, 1930). The CTST/Eckart calculations are performed with the KiSThelP 2019 program (Canneaux et al., 2013).

The rate coefficients of each elementary pathway included in the initiation reactions of distinct SCIs with HCOOH are calculated in the temperature range of 273-400 K, as listed in Table S3-S6. As shown in Table S3, the total rate coefficients $k_{tot\text{-}CH2OO}$ *of* CH_2OO *reaction with HCOOH are in excess of* 1.0×10^{-10} *cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$*, and they exhibit a slightly negative temperature dependence in the temperature range studied.* $k_{tot\text{-}CH2OO}$*is estimated to be* 1.4×10^{-10}*cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$ *at 298 K, which is in good agreement with the experimental values reported by Welz et al. (2014) (*$[1.1 \pm 0.1] \times 10^{-10}$*), Chung et al. (2019) (*$[1.4 \pm 0.3] \times 10^{-10}$*), and Peltola et al. (2020) (*$[1.0 \pm 0.03] \times 10^{-10}$*).* $k(TS_{ent1})$ *is approximately equal to* $k_{tot\text{-}CH2OO}$ *in the whole temperature range, and it decreases in the range of* 1.7×10^{-10} *(273 K) to* 1.2×10^{-10} *(400 K) cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$ *with increasing temperature.* $k(TS_{ent1})$ *is several orders of magnitude greater than* $k(TS_{ent2})$*,* $k(TS_{ent3})$ *and* $k(TS_{ent4})$ *over the temperature range from 273 to 400 K. The result again shows that the barrierless 1,4 O-H insertion reaction is predominant.*

Equivalent to the case of CH_2OO reaction with HCOOH, the rate coefficient of each elementary pathway involved in the anti-CH_3CHOO + HCOOH reaction also decreases with the temperature increasing (Table S4). This table shows that Entry 1 is kinetically favored over Entry 2, 3 and 4, and Entry 2 is competitive with Entry 4 in the range 273-400 K. Similar conclusion is also obtained from the results of the rate coefficients for the reactions of syn-CH_3CHOO and $(CH_3)_2COO$ with HCOOH that Entry 1 is the dominant pathway (Table S5-S6). It deserves mentioning that the competition of Entry 2 is significantly greater than that of Entry 4 in the syn-CH_3CHOO + HCOOH and $(CH_3)_2COO$ + HCOOH systems. At ambient temperature, the total rate coefficients of HCOOH reactions with anti-CH_3CHOO, syn-CH_3CHOO and $(CH_3)_2COO$ are estimated to be 5.9, 2.7 and 4.8 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively, which are consistent with the prior experimental measurements of 5 ± 3, 2.5 ± 0.3 and 4.5 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Welz et al., 2014; Chung et al., 2019; Sipilä et al., 2014).

- The trend in exothermicity with substitution pattern (p.8-9) should be explained.

Response: Based on the Reviewer's suggestion, the relevance explanations on the trend in exothermicity have been added in the revised manuscript. The exothermicity of 1,4 O-H insertion reactions of distinct SCIs with HCOOH is assessed by the reaction enthalpy (), which is defined as the difference between the enthalpies of formation () of the products and reactants (). To the best of our knowledge, there are no literature values available on the enthalpies of formation of carbonyl oxides and hydroperoxide esters except the simplest carbonyl oxide CH_2OO. Therefore, the isodesmic reaction method is adopted to obtain the enthalpies of formation, and the results are listed in Table S2. An isodesmic reaction is a hypothetical reaction, in which the type of chemical bonds in the reactants is the similar as that of chemical bonds in the products. The following isodesmic reaction is constructed because the experimental values of H_2, CH_4 and H_2O are available ((H_2) = 0.00 kcal·mol^{-1}; (CH_4) = -17.82 kcal·mol^{-1}; (H_2O) = -57.79 kcal·mol^{-1}).

(4)

As seen in Table S2, the enthalpy of formation of CH_2OO is calculated to be 23.23 kcal·mol^{-1}, which is in good agreement with the available literature values (Karton et al., 2013; Chen et al., 2016). This result implies that the theoretical method employed herein is reasonable to predict the thermochemical parameters. The enthalpies of formation of carbonyl oxides and hydroperoxide esters significantly decrease with increasing the number of methyl groups. Notably, the decreased values in the enthalpies of formation of carbonyl oxides are greater than those of hydroperoxide esters under the condition of the same number of methyl groups. For example, the enthalpy of formation of *anti*-CH_3CHOO decreases by 12.95 kcal·mol^{-1} compared to the enthalpy of formation of CH_2OO, and the enthalpy of formation of Pent1b decreases by 12.12 kcal·mol^{-1} compared to the enthalpy of formation of Pent1a. The reaction enthalpies decrease in the order of -44.69 (CH_2OO + HCOOH □ Pent1a) < -43.86 (*anti*-CH_3CHOO + HCOOH □ Pent1b) < -38.13 (*syn*-CH_3CHOO + HCOOH □ Pent1c) < -37.12 kcal·mol^{-1} ($(CH_3)_2COO$ + HCOOH □ Pent1d), indicating that the reaction enthalpies are highly dependent on the number and location of methyl groups. The trend in reaction enthalpies is consistent with the trend in the enthalpies of formation of carbonyl oxides. The reason might be attributed to the decreased values in the enthalpies of formation of carbonyl oxides greater than those of hydroperoxide esters under the condition of the same number of methyl groups.

Table S2 Enthalpies of formation () for the various carbonyl oxides and hydroperoxide esters computed at the CCSD(T)//M06-2X/6-311+G(2df,2p) level of theory

Species	Cal (kcal·mol^{-1})	Refs. (kcal·mol^{-1})
CH_2OO	23.23	22.92[a]
		24.59[b]
anti-CH_3OO	10.28	
syn-CH_3CHOO	6.73	
$(CH_3)_2COO$	-6.77	
HCOOH		-90.62 (exp)
$HC(O)OCH_2OOH$ (Pent1a)	-112.08	
$HC(O)OCH(CH_3)OOH$ (Pent1b)	-124.20	
$HC(O)OCH(CH_3)OOH$ (Pent1c)	-122.02	
$HC(O)OC(CH_3)_2OOH$ (Pent1d)	-134.51	

Exp is taken from NIST Chemistry Webbook

[a] the value is obtained at the G4 level of theory (Chen et al., 2016)

[b] the value is obtained at the W3-F12 level of theory (Karton et al., 2013)

Corresponding descriptions have been added in the page 9 line 240-247 and page 10 line 248-271 of the revised manuscript:

The exothermicity of 1,4 O-H insertion reactions of distinct SCIs with HCOOH is assessed by the reaction enthalpy (), which is defined as the difference between the enthalpies of formation () of the products and reactants (). To the best of our knowledge, there are no literature values available on the enthalpies of formation of carbonyl oxides and hydroperoxide esters except the simplest carbonyl oxide CH_2OO*. Therefore, the isodesmic reaction method is adopted to obtain the enthalpies of formation, and the results are listed in Table S2. An isodesmic reaction is a hypothetical reaction, in which the type of chemical bonds in the reactants is the similar as that of chemical bonds in the products. The following isodesmic reaction is constructed because the experimental values of* H_2*,* CH_4 *and* H_2O *are available ((*H_2*) = 0.00 kcal·mol*$^{-1}$*; (*CH_4*) = -17.82 kcal·mol*$^{-1}$*; (*H_2O*) = -57.79 kcal·mol*$^{-1}$*).*

(4)

As seen in Table S2, the enthalpy of formation of CH_2OO *is calculated to be 23.23 kcal·mol*$^{-1}$*, which is in good agreement with the available literature values (Chen et al., 2016; Karton et al., 2013). This result implies that the theoretical method employed herein is reasonable to predict the thermochemical parameters. The enthalpies of formation of carbonyl oxides and hydroperoxide esters significantly decrease with increasing the number of methyl groups. Notably, the decreased values in the enthalpies of formation of carbonyl oxides are greater than those of hydroperoxide esters under the condition of the same number of methyl groups. For example, the enthalpy of formation of anti-*CH_3CHOO *decreases by 12.95 kcal·mol*$^{-1}$ *compared to the enthalpy of formation of* CH_2OO*, and the enthalpy of formation of Pent1b decreases by 12.12 kcal·mol*$^{-1}$ *compared to the enthalpy of formation of Pent1a. The reaction enthalpies decrease in the order of -44.69 (*CH_2OO *+ HCOOH □ Pent1a) < -43.86 (anti-*CH_3CHOO *+ HCOOH □ Pent1b) < -38.13 (syn-*CH_3CHOO *+ HCOOH □ Pent1c) < -37.12 kcal·mol*$^{-1}$ *((*$(CH_3)_2COO$ *+ HCOOH □ Pent1d), indicating that the reaction enthalpies are highly dependent on the number and location of methyl groups. The trend in reaction enthalpies is consistent with the trend in the enthalpies of formation of carbonyl oxides. The reason might be attributed to the decreased values in the enthalpies of formation of carbonyl oxides greater than those of hydroperoxide esters under the condition of the same number of methyl groups.*

- The analysis of possible bimolecular CI reactions (p.21) should be extended to the three substituted CIs.

Response: Kalinowski et al. has comfirmed that the central CO bond of carbonyl oxides is a double bond, while the terminal OO bond is a single bond (Kalinowski et al., 2014). It is therefore that the maximum degree of substitution of carbonyl oxides is two. To further evaluate the relative importance of the complex SCIs reactions with coreactant, the bimolecular reactions of methyl vinyl ketone oxide (MVK-OO) with H_2O, HCOOH, SO_2 and HPMF have been considered in the revised manuscript. MVK-OO, formed with 21 to 23% yield from the ozonolysis of isoprene, is a four carbon, asymmetric, resonance-stabilized Criegee intermediate (Barber et al., 2018). MVK-OO has four conformers, *syn-trans-*, *syn-cis-*, *anti-trans-*, and *anti-cis-* as shown in Fig. S10. Herein, *syn* and *anti* refer to the orientation of the -CH_3 group relative to the terminal oxygen of MVK-OO, whereas *cis* and *trans* refer to the orientation of the C_8=C_9 bond relative to the C_1=O_2 bond. According to the results shown in the Fig. S10, the lowest-energy conformer is *syn-trans*-MVK-OO, which is lower than *syn-cis*-, *anti-trans*-, and *anti-cis*-MVK-OO by 1.42, 2.43 and 2.69 kcal·mol^{-1}, respectively. Therefore, the lowest-energy conformer *syn-trans*-MVK-OO is selected as the model compound to study its bimolecular reactions. As shown in Table 2, the rate coefficient of H_2O reaction with *syn-trans*-MVK-OO is lower than with other SCIs by 2 to 3 orders of magnitude. The reason is likely to be that the existence of methyl and vinyl groups hinders the occurrence of bimolecular reaction with water vapour. Consequently, a fraction of *syn-trans*-MVK-OO may survive in the presence of water vapour and react with other species. $k_{\text{eff(MVK-OO+H2O)}}$ is nearly identical to $k_{\text{eff(MVK-OO+HCOOH)}}$, which is greater than $k_{\text{eff(MVK-OO+SO2)}}$ and $k_{\text{eff(MVK-OO+HPMF)}}$ when the concentration of HPMF is the same as that of HCOOH. $k_{\text{eff(MVK-OO+H2O)}}$ and $k_{\text{eff(MVK-OO+HCOOH)}}$ are greater than $k_{\text{eff(MVK-OO+SO2)}}$, which, in turn, are greater than $k_{\text{eff(MVK-OO+HPMF)}}$ when the concentration of HPMF is equal to that of SCIs. Based on the above discussions, it can be concluded that the relative importance of carbonyl oxides reactions with hydroperoxide esters is significantly dependent on the concentrations of hydroperoxide esters. These reactions may play a certain role in the formation of organic new particle in some regions where low concentration of water vapour and high concentration of hydroperoxide esters occur.

	trans	cis
syn	0.00	1.42
anti	2.43	2.69

Figure S10. The optimized geometries and relative energies (kcal·mol^{-1}) computed for the four conformers of MVK-oxide. Geometries are optimized at the M06-2X/6-311+g(2df,2p) level of theory. Single point energies are calculated at the CCSD(T)/6-311+g(2df,2p) level of theory.

Corresponding descriptions have been added in the page 24 line 611-619 and page 25 line 620-636 of the revised manuscript:

To further evaluate the relative importance of the complex SCIs reactions with coreactant, the bimolecular reactions of methyl vinyl ketone oxide (MVK-OO) with H_2O, HCOOH, SO_2, and HPMF are considered. MVK-OO, formed with 21 to 23% yield from the ozonolysis of isoprene, is a four carbon, asymmetric, resonance-stabilized Criegee intermediate

(Barber et al., 2018). MVK-OO has four conformers, syn-trans-, syn-cis-, anti-trans-, and anti-cis- as shown in Fig. S10. Herein, syn and anti refer to the orientation of the –CH_3 *group relative to the terminal oxygen of MVK-OO, whereas cis and trans refer to the orientation of the* $C_8=C_9$ *bond relative to the* $C_1=O_2$ *bond. According to the results shown in the Fig. S10, the lowest-energy conformer is syn-trans-MVK-OO, which is lower than syn-cis-, anti-trans-, and anti-cis-MVK-OO by 1.42, 2.43 and 2.69 kcal·mol*$^{-1}$*, respectively. Therefore, the lowest-energy conformer syn-trans-MVK-OO is selected as the model compound to study its bimolecular reactions. As shown in Table 2, the rate coefficient of* H_2O *reaction with syn-trans-MVK-OO is lower than with other SCIs by 2 to 3 orders of magnitude. The reason is likely to be that the existence of methyl and vinyl groups hinders the occurrence of bimolecular reaction with water vapour. Consequently, a fraction of syn-trans-MVK-OO may survive in the presence of water vapour and react with other species.* $k_{eff(MVK\text{-}OO+H2O)}$ *is nearly identical to* $k_{eff(MVK\text{-}OO+HCOOH)}$*, which is greater than* $k_{eff(MVK\text{-}OO+SO2)}$ *and* $k_{eff(MVK\text{-}OO+HPMF)}$ *when the concentration of HPMF is the same as that of HCOOH.* $k_{eff(MVK\text{-}OO+H2O)}$ *and* $k_{eff(MVK\text{-}OO+HCOOH)}$ *are greater than* $k_{eff(MVK\text{-}OO+SO2)}$*, which, in turn, are greater than* $k_{eff(MVK\text{-}OO+HPMF)}$ *when the concentration of HPMF is equal to that of SCIs. Based on the above discussions, it can be concluded that the relative importance of carbonyl oxides reactions with hydroperoxide esters is significantly dependent on the concentrations of hydroperoxide esters. These reactions may play a certain role in the formation of organic new particle in some regions where low concentration of water vapour and high concentration of hydroperoxide esters occur.*

- Since the CI is clearly the limiting reactant in the CI + HCOOH reaction, the atmospheric concentration of HPMF (and the other hydroperoxy esters) is much better estimated to be the CI concentration. (This, of course, will greatly lower the predicted pseudo-first-order rate constants for the CI + HPMF reaction.)

Response: Based on the Reviewer's suggestion, the relevance explanations on the predicted pseudo-first-order rate constants have been added in the revised manuscript. It is of interest to assess whether the reactions of distinct SCIs with HPMF can compete well with the losses to reactions with trace species (e.g., H_2O, HCOOH and SO_2), because it is well known that the reactions with trace species are expected to be the dominant chemical sinks for SCIs in the atmosphere (Taatjes et al., 2013; Long et al., 2016). The reported concentrations of coreactant, the rate coefficients *k*, and the effective pseudo-first-order rate constants ($k_{eff} = k$[coreactant]) for distinct SCI reactions with H_2O, HCOOH, SO_2 and HPMF are summarized in Table 2. As seen in Table 2, the rate coefficient of a particular SCI reaction with trace species is strongly dependent on its structure. The methyl group substitution may alter the rate coefficient by several to tens of times. The atmospheric concentrations of H_2O, HCOOH and SO_2 in the tropical forest environments are measured to be 3.9-6.1 × 10^{17}, 5.0-10 × 10^{10}, and 1.7-9.0 × 10^{10} molecules cm^{-3}, respectively (Vereecken, 2012). For the reactions of CH_2OO with H_2O, HCOOH, and SO_2, the experimental rate coefficients are determined to be < 1.5 × 10^{-15}, [1.1 ± 0.1] × 10^{-10}, and [3.9 ± 0.7] × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively (Welz et al., 2012 and 2014; Chao et al., 2015), which translate into $k_{eff(CH2OO+H2O)}$, $k_{eff(CH2OO+HCOOH)}$ and $k_{eff(CH2OO+SO2)}$ of 5.9-9.2 × 10^2, 5.5-11, and 0.7-3.5 s^{-1}, respectively. The result reveals that the reaction of CH_2OO with H_2O is the most important bimolecular reaction. $k_{eff(CH2OO+HCOOH)}$ is greater by a factor of 3-8 than $k_{eff(CH2OO+SO2)}$, indicating that the reaction of CH_2OO with HCOOH is favored over reaction with SO_2. Similar conclusion is also obtained from the results of k_{eff} for the reactions of *anti*-CH_3CHOO, *syn*-CH_3CHOO and $(CH_3)_2COO$ with H_2O, HCOOH and SO_2 that SCIs reactions with H_2O are faster than with HCOOH, which, in turn, are faster than with SO_2.

According to the results shown in the Table 2, the room temperature rate coefficient for the reaction of CH_2OO with HPMF is calculated to be 2.7 × 10^{-11} cm^3 molecule^{-1} s^{-1}.

However, to the best of our knowledge, the atmospheric concentration of HPMF has not been reported up to now. If we assume that the concentration of HPMF is the same as that of HCOOH, $k_{\mathrm{eff(CH2OO+HPMF)}}$ is estimated to be 1.4-2.7 s^{-1}, which is significantly lower than $k_{\mathrm{eff(CH2OO+H2O)}}$ and $k_{\mathrm{eff(CH2OO+HCOOH)}}$. $k_{\mathrm{eff(CH2OO+HPMF)}}$ is nearly identical to $k_{\mathrm{eff(CH2OO+SO2)}}$, indicating that the CH_2OO + HPMF reaction is competitive with the CH_2OO + SO_2 system. Previous model-measurement studies have estimated the surface-level SCIs concentrations in the range of 1.0×10^4 to 1.0×10^5 molecules cm^{-3} (Khan et al., 2018; Novelli et al., 2017). If we assume that the concentration of HPMF is equal to that of SCIs, $k_{\mathrm{eff(CH2OO+HPMF)}}$ is calculated to be $2.7\text{-}27 \times 10^{-7}$ s^{-1}, which is several orders of magnitude lower than $k_{\mathrm{eff(CH2OO+H2O)}}$, $k_{\mathrm{eff(CH2OO+HCOOH)}}$ and $k_{\mathrm{eff(CH2OO+SO2)}}$. This result indicates that the reaction of CH_2OO with HPMF is of less importance. Similar conclusion is also obtained from the reactions of *anti*-CH_3CHOO, *syn*-CH_3CHOO and $(CH_3)_2COO$ with HPMF. Based on the above discussions, it can be concluded that the relative importance of carbonyl oxides reactions with hydroperoxide esters is significantly dependent on the concentrations of hydroperoxide esters.

Table 2 The reported concentrations of coreactant, the rate coefficients *k*, and the effective pseudo-first-order rate constants ($k_{\mathrm{eff}} = k$[coreactant]) for distinct SCI reactions with HPMF, H_2O, HCOOH and SO_2 at the tropical forest environments

SCIs	Coreactant	[Coreactant] (molecules cm^{-3})	k (cm^3 $molecule^{-1}$ s^{-1})	k_{eff} (s^{-1})	Reference
CH_2OO	H_2O	$3.9\text{-}6.1 \times 10^{17}$	$< 1.5 \times 10^{-15}$	$5.9\text{-}9.2 \times 10^{2}$	Chao et al., (2015)
HCOOH	$5.0\text{-}10.0 \times 10^{10}$	$[1.1 \pm 0.1] \times 10^{-10}$	5.5-11	Welz et al., (2014)	
SO_2	$1.7\text{-}9.0 \times 10^{10}$	$[3.9 \pm 0.7] \times 10^{-11}$	0.7-3.5	Welz et al., (2012)	
HPMF	-	2.7×10^{-11}	-	This work	
anti-CH_3CHOO	H_2O	$3.9\text{-}6.1 \times 10^{17}$	$[1.0 \pm 0.4] \times$	$3.9\text{-}6.1 \times 10^{3}$	Taatjes et al.,

			10^{-14}		(2013)
HCOOH	5.0-10.0 × 10^{10}	[5 ± 3] × 10^{-10}	25.0-50.0	Welz et al., (2014)	
SO_2	1.7-9.0 × 10^{10}	[6.7 ± 1.0] × 10^{-11}	1.1-6.0	Taatjes et al., (2013)	
HPMF	-	3.3 × 10^{-10}	-	This work	
syn-CH_3CHOO	H_2O	3.9-6.1 × 10^{17}	$< 4.0 \times 10^{-15}$	1.6-2.4 × 10^3	Taatjes et al., (2013)
HCOOH	5.0-10.0 × 10^{10}	[2.5 ± 0.3] × 10^{-10}	12.5-25.0	Welz et al., (2014)	
SO_2	1.7-9.0 × 10^{10}	[2.4 ± 0.3] × 10^{-11}	0.4-2.2	Taatjes et al., (2013)	
HPMF	-	1.7 × 10^{-13}	-	This work	
$(CH_3)_2COO$	H_2O	3.9-6.1 × 10^{17}	$< 1.5 \times 10^{-16}$	58.5-91.5	Huang et al., (2015)
HCOOH	5.0-10.0 × 10^{10}	4.5 × 10^{-10}	22.5-45.0	Sipilä et al., (2014)	

	SO_2	$1.7\text{-}9.0 \times 10^{10}$	1.3×10^{-10}	2.2-11.7	Huang et al., (2015)
	HPMF	-	2.2×10^{-11}	-	This work
syn-trans-MVK-OO	H_2O	$3.9\text{-}6.1 \times 10^{17}$	$< 4.0 \times 10^{-17}$	15.6-24.4	Caravan et al., (2020)
	HCOOH	$5.0\text{-}10.0 \times 10^{10}$	$[3.0 \pm 0.1] \times 10^{-10}$	15.0-30.0	Caravan et al., (2020)
	SO_2	$1.7\text{-}9.0 \times 10^{10}$	$[4.2 \pm 0.6] \times 10^{-11}$	0.7-3.8	Caravan et al., (2020)
	HPMF	-	3.0×10^{-11}	-	This work

Corresponding descriptions have been added in the page 23 line 573-590 and page 24 line 591-610 of the revised manuscript:

It is of interest to assess whether the reactions of distinct SCIs with HPMF can compete well with the losses to reactions with trace species (e.g., H_2O, HCOOH and SO_2), because it is well known that the reactions with trace species are expected to be the dominant chemical sinks for SCIs in the atmosphere (Taatjes et al., 2013; Long et al., 2016). The reported concentrations of coreactant, the rate coefficients k, and the effective pseudo-first-order rate constants (k_{eff} = k[coreactant]) for distinct SCI reactions with H_2O, HCOOH, SO_2, and HPMF are summarized in Table 2. As seen in Table 2, the rate coefficient of a particular SCI reaction with trace species is strongly dependent on its structure. The methyl group substitution may alter the rate coefficient by several to tens of times. The atmospheric concentrations of H_2O, HCOOH and SO_2 in the tropical forest environments are measured to be $3.9\text{-}6.1 \times 10^{17}$, $5.0\text{-}10 \times 10^{10}$, and $1.7\text{-}9.0 \times 10^{10}$ molecules cm^{-3}, respectively (Vereecken, 2012). For the reactions of CH_2OO with H_2O, HCOOH, and SO_2, the experimental rate coefficients are determined to be $< 1.5 \times 10^{-15}$, $[1.1 \pm 0.1] \times 10^{-10}$, and $[3.9 \pm 0.7] \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively (Welz et al., 2012 and 2014; Chao et al., 2015), which translate into $k_{eff(CH2OO+H2O)}$, $k_{eff(CH2OO+HCOOH)}$ and $k_{eff(CH2OO+SO2)}$ of $5.9\text{-}9.2 \times 10^2$, 5.5-11, and 0.7-3.5 s^{-1}, respectively. The result reveals that the reaction of CH_2OO with H_2O is the most important bimolecular reaction. $k_{eff(CH2OO+HCOOH)}$ is greater by a factor of 3-8 than $k_{eff(CH2OO+SO2)}$, indicating that the reaction of CH_2OO with HCOOH is favored over reaction with SO_2. Similar conclusion is also obtained from the results of k_{eff} for the reactions of anti-CH_3CHOO, syn-CH_3CHOO and

$(CH_3)_2COO$ with H_2O, HCOOH and SO_2 that SCIs reactions with H_2O are faster than with HCOOH, which, in turn, are faster than with SO_2.

According to the results shown in the Table 2, the room temperature rate coefficient for the reaction of CH_2OO with HPMF is calculated to be 2.7 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. However, to the best of our knowledge, the atmospheric concentration of HPMF has not been reported up to now. If we assume that the concentration of HPMF is the same as that of HCOOH, $k_{eff(CH2OO+HPMF)}$ is estimated to be 1.4-2.7 s^{-1}, which is significantly lower than $k_{eff(CH2OO+H2O)}$ and $k_{eff(CH2OO+HCOOH)}$. $k_{eff(CH2OO+HPMF)}$ is nearly identical to $k_{eff(CH2OO+SO2)}$, indicating that the CH_2OO + HPMF reaction is competitive with the CH_2OO + SO_2 system. Previous model-measurement studies have estimated the surface-level SCIs concentrations in the range of 1.0 × 10^4 to 1.0 × 10^5 molecules cm^{-3} (Khan et al., 2018; Novelli et al., 2017). If we assume that the concentration of HPMF is equal to that of SCIs, $k_{eff(CH2OO+HPMF)}$ is calculated to be 2.7-27 × 10^{-7} s^{-1}, which is several orders of magnitude lower than $k_{eff(CH2OO+H2O)}$, $k_{eff(CH2OO+HCOOH)}$ and $k_{eff(CH2OO+SO2)}$. This result indicates that the reaction of CH_2OO with HPMF is of less importance. Similar conclusion is also obtained from the reactions of anti-CH_3CHOO, syn-CH_3CHOO and $(CH_3)_2COO$ with HPMF. Based on the above discussions, it can be concluded that the relative importance of carbonyl oxides reactions with hydroperoxide esters is significantly dependent on the concentrations of hydroperoxide esters.

- Since a big motivation for the computations is the potential for CI + hydroperoxy ester reactions to lead to SOA, there should be some specific discussion, perhaps buttressed by rough calculations, of how many cycles of CI addition are required before a given adduct is expected to have low volatility. The approach of Chhantyal-Pun et al. (ACS Earth Space Chem. 2018, 2, 8, 833-842) is an example of the approach the authors should take.

Response: Based on the Reviewer’s suggestion, the vapour pressure and volatility of adduct products formed from the successive reactions of SCIs with hydroperoxide esters have been added in the revised manuscript. The assessment of Barley and McFiggans (2010) and O'Meara et al. (2014) found that the combination of boiling point estimation from Nannoolal et al. (2004) and vapour pressure estimation from Nannoolal et al. (2008) gives the lowest mean bias error of vapour pressure for atmospherically relevant compounds. Therefore, the saturated vapour pressure (P^0) of adduct products at room temperature is estimated by using the Nannoolal-Nannoolal method, and the results are listed in Table S10.

From Table S10, it can be seen that the P^0 of adduct products involved in the successive reactions of CH_2OO with HCOOH increases first and then decreases with increasing the number of CH_2OO. The P^0 of the adduct product $HC(O)O(CH_2OO)_3H$ is maximum when the number of CH_2OO is equal to three. The P^0 of adduct products included in the successive reactions of *anti*-CH_3CHOO with HCOOH decreases significantly as the number of *anti* -CH_3CHOO is increased. Similar phenomenon is also observed from the successive reactions of *syn*-CH_3CHOO and $(CH_3)_2COO$ with HCOOH. Notably, the P^0 of adduct products decreases obviously when the size of SCIs increases. For example, the P^0 of the adduct product $HC(O)O(CH_2OO)_3H$ in the nCH_2OO + HCOOH reaction is estimated to be 4.43 × 10^{-3} atm, which is greater than those of the corresponding adduct products in the n*anti*-CH_3CHOO + HCOOH (7.12 × 10^{-4}), n*syn*-CH_3CHOO + HCOOH (7.12 × 10^{-4}), and n$(CH_3)_2COO$ + HCOOH (1.27 × 10^{-4}) reactions by 6.22, 6.22 and 34.88 times, respectively.

A classify scheme of various organic compounds is based on their volatility, as presented by Donahue et al. (2012) The volatility of organic compounds is described by their effective saturation concentration. The saturated concentrations (c^0) of adduct products formed from the successive reactions of SCIs with HCOOH are predicted by using the SIMPOL.1 method proposed by Pankow and Asher (2008), and the results are listed in Table S10. As shown in Table S10, the c^0 of adduct products involved in the nCH_2OO + HCOOH reaction decreases with increasing the number of CH_2OO. According to the Volatility Basis Set (VBS) of organic compounds (Donahue et al., 2012), these adduct products belong to volatile organic compounds (VOC, $c^0 > 3 \times 10^6$ ug/m^3). Similarly, the c^0 of adduct products included in the n*anti*-CH_3CHOO + HCOOH, n*syn*-CH_3CHOO + HCOOH, and n$(CH_3)_2COO$ + HCOOH reactions decreases when the number of SCIs increases. It deserves mentioning that the adduct products in the n*anti*-CH_3CHOO + HCOOH and n*syn*-CH_3CHOO + HCOOH reactions belong to intermediate volatility organic compounds (IVOC, $300 < c^0 < 3 \times 10^6$ ug/m^3) when the number of SCIs is equal to five. However, the adduct products in the n$(CH_3)_2COO$ + HCOOH reaction become IVOC when the number of $(CH_3)_2COO$ is greater than or equal to two. Based on the above discussions, it can be concluded that the volatility of adduct products is significantly affected by the number and size of SCIs in the successive reaction of SCIs with HCOOH.

Table S10 Predicted saturated vapour pressure (P^0) and saturated concentrations (c^0) for the adduct products of the successive reactions of SCIs with HCOOH

	formula	P^0 (atm)	c^0 (ug/m^3)
n CH_2OO + HCOOH			
n = 1	$HC(O)OCH_2OOH$	2.12×10^{-3}	7.86×10^7
n = 2	$HC(O)O(CH_2OO)_2H$	3.80×10^{-3}	3.99×10^7
n = 3	$HC(O)O(CH_2OO)_3H$	4.43×10^{-3}	3.91×10^7
n = 4	$HC(O)O(CH_2OO)_4H$	4.21×10^{-3}	3.29×10^7
n = 5	$HC(O)O(CH_2OO)_5H$	3.59×10^{-3}	2.12×10^7

n *anti*-CH_3CHOO + $HCOOH$			
n = 1	$HC(O)OCH(CH_3)OOH$	1.25×10^{-3}	8.32×10^{6}
n = 2	$HC(O)O(CH(CH_3)OO)_2H$	1.13×10^{-3}	7.57×10^{6}
n = 3	$HC(O)O(CH(CH_3)OO)_3H$	7.12×10^{-4}	6.49×10^{6}
n = 4	$HC(O)O(CH(CH_3)OO)_4H$	3.90×10^{-4}	4.50×10^{6}
n = 5	$HC(O)O(CH(CH_3)OO)_5H$	2.01×10^{-4}	2.81×10^{6}
n *syn*-CH_3CHOO + $HCOOH$			
n = 1	$HC(O)OCH(CH_3)OOH$	1.25×10^{-3}	8.32×10^{6}
n = 2	$HC(O)O(CH(CH_3)OO)_2H$	1.13×10^{-3}	7.57×10^{6}
n = 3	$HC(O)O(CH(CH_3)OO)_3H$	7.12×10^{-4}	6.49×10^{6}

n = 4	$HC(O)O(CH(CH_3)OO)_4H$	3.90×10^{-4}	4.50×10^{6}
n = 5	$HC(O)O(CH(CH_3)OO)_5H$	2.01×10^{-4}	2.81×10^{6}
n $(CH_3)_2COO$ + $HCOOH$			
n = 1	$HC(O)OC(CH_3)_2OOH$	7.23×10^{-4}	3.50×10^{6}
n = 2	$HC(O)O(C(CH_3)_2OO)_2H$	3.50×10^{-4}	2.74×10^{6}
n = 3	$HC(O)O(C(CH_3)_2OO)_3H$	1.27×10^{-4}	1.38×10^{6}
n = 4	$HC(O)O(C(CH_3)_2OO)_4H$	4.27×10^{-5}	5.90×10^{5}
n = 5	$HC(O)O(C(CH_3)_2OO)_5H$	1.40×10^{-5}	2.36×10^{5}

Corresponding descriptions have been added in the page 27 line 644-671 and page 28 line 672-682 of the revised manuscript:

The assessment of Barley and McFiggans (2010) and O'Meara et al. (2014) found that the combination of boiling point estimation from Nannoolal et al. (2004) and vapour pressure estimation from Nannoolal et al. (2008) gives the lowest mean bias error of vapour *pressure for atmospherically relevant compounds. Therefore, the saturated vapour pressure (P^0) of adduct products at room temperature is estimated by using the Nannoolal-Nannoolal method, and the results are listed in Table S10. From Table S10, it can be seen that the P^0 of adduct products involved in the successive reactions of CH_2OO with HCOOH increases first and then decreases with increasing the number of CH_2OO. The P^0 of the adduct product $HC(O)O(CH_2OO)_3H$ is maximum when the number of CH_2OO is equal to three. The P^0 of adduct products included in the successive reactions of anti-CH_3CHOO with HCOOH decreases significantly as the number of anti-CH_3CHOO is increased. Similar phenomenon is also observed from the successive reactions of syn-CH_3CHOO and $(CH_3)_2COO$ with HCOOH. Notably, the P^0 of adduct products decreases obviously when the size of SCIs increases. For example, the P^0 of the adduct product $HC(O)O(CH_2OO)_3H$ in the nCH_2OO + HCOOH reaction is estimated to be 4.43×10^{-3} atm, which is greater than those of the corresponding adduct products in the nanti-CH_3CHOO + HCOOH (7.12×10^{-4}), nsyn-CH_3CHOO + HCOOH (7.12×10^{-4}), and n$(CH_3)_2COO$ + HCOOH (1.27×10^{-4}) reactions by 6.22, 6.22 and 34.88 times, respectively.*

A classify scheme of various organic compounds is based on their volatility, as presented by Donahue et al. (2012) The volatility of organic compounds is described by their effective saturation concentration. The saturated concentrations (c^0) of adduct products formed from the successive reactions of SCIs with HCOOH are predicted by using the SIMPOL.1 method proposed by Pankow and Asher (2008), and the results are listed in Table S10. As shown in Table S10, the c^0 of adduct products involved in the nCH_2OO + HCOOH reaction decreases with increasing the number of CH_2OO. According to the Volatility Basis Set (VBS) of organic compounds (Donahue et al., 2012), these adduct products belong to VOC ($c^0 > 3 \times 10^6$ ug/m^3). Similarly, the c^0 of adduct products included in the nanti-CH_3CHOO + HCOOH, nsyn-CH_3CHOO + HCOOH, and n$(CH_3)_2COO$ + HCOOH reactions decreases when the number of SCIs increases. It deserves mentioning that the adduct products in the nanti-CH_3CHOO + HCOOH and nsyn-CH_3CHOO + HCOOH reactions belong to intermediate volatility organic compounds (IVOC, $300 < c^0 < 3 \times 10^6$ ug/m^3) when the number of SCIs is equal to five. However, the adduct products in the n$(CH_3)_2COO$ + HCOOH reaction become IVOC when the number of $(CH_3)_2COO$ is greater than or equal to two. Based on the above discussions, it can be concluded that the volatility of adduct products is significantly affected by the number and size of SCIs in the successive reaction of SCIs with HCOOH.

- On p. 6, line 145: "saddle point" should be "minimum".

Response: The word "saddle point" has been replaced by "minimum" in the revised manuscript.

- On p. 6, line 162: "precision" should be "accuracy".

Response: The word "precision" has been replaced by "accuracy" in the revised manuscript.

- On p. 7, line 182: "decomposes" should be "rearranges".

Response: The word "decomposes" has been replaced by "rearranges" in the revised manuscript.

- On p. 14, lines 341-342, use a non-breaking hyphen.

Response: A non-breaking hyphen has been used in the revised manuscript.

- On p. 15, line 372, "intermolecular" should be "intramolecular".

Response: The word "intermolecular" has been replaced by "intramolecular" in the revised manuscript.

- On p. 17, lines 413-414, use a non-breaking hyphen.

Response: A non-breaking hyphen has been used in the revised manuscript.

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