

Atmos. Chem. Phys. Discuss., author comment AC1  
<https://doi.org/10.5194/acp-2022-376-AC1>, 2022  
© Author(s) 2022. This work is distributed under  
the Creative Commons Attribution 4.0 License.

## 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

---

Prof. Yu Huang

State Key Lab of Loess and Quaternary Geology

Institute of Earth Environment, Chinese Academy of Sciences, Xi'an,  
710061, China

Tel./Fax: (86) 29-62336261

E-mail: [huangyu@ieecas.cn](mailto:huangyu@ieecas.cn)

Aug. 25, 2022

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,  $V(R) = D_e \{1 - \exp[-\beta(R - R_e)]\}^2$ , 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  $V_{\text{anisotropy}} = V_0[1 - \cos^2(\theta_1 - \theta_{1e}) \times \cos^2(\theta_2 - \theta_{2e})]$  (Raghunath et al., 2017). Here,  $V_0$  is the stretching potential, which stands for by a Morse potential,  $\theta_1$  and  $\theta_{1e}$  represent the rotational angle between fragment 1 and the reference axis and the equilibrium bond angle of fragment 1,  $\theta_2$  and  $\theta_{2e}$  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 KiSTheP 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  $5.0 \times 10^{10}$  molecules  $\text{cm}^{-3}$  in the simulation, which is taken from the typical concentration of HCOOH in the tropical forest environments (Vereecken, 2012).  $\text{N}_2$  is applied as the buffer gas. A single exponential down model is employed to simulate the collision transfer ( $\langle \Delta E \rangle_{\text{down}} = 200 \text{ cm}^{-1}$ ). 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  $k_{\text{tot-CH}_2\text{OO}}$  of CH<sub>2</sub>OO reaction with HCOOH are in excess of  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and they exhibit a slightly negative temperature dependence in the temperature range studied.  $k_{\text{tot-CH}_2\text{OO}}$  is estimated to be  $1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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) ( $[1.0 \pm 0.03] \times 10^{-10}$ ).  $k(\text{TS}_{\text{ent}1})$  is approximately equal to  $k_{\text{tot-CH}_2\text{OO}}$  in the whole temperature range, and it decreases in the range of  $1.7 \times 10^{-10}$  (273 K) to  $1.2 \times 10^{-10}$  (400 K)  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with increasing temperature.  $k(\text{TS}_{\text{ent}1})$  is several orders of magnitude greater than  $k(\text{TS}_{\text{ent}2})$ ,  $k(\text{TS}_{\text{ent}3})$  and  $k(\text{TS}_{\text{ent}4})$  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<sub>3</sub>CHOO, *syn*-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO (Table S4-S6). At ambient temperature, the total rate coefficients of HCOOH reactions with *anti*-CH<sub>3</sub>CHOO, *syn*-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO are estimated to be 5.9, 2.7 and  $4.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, which are consistent with the prior experimental measurements of  $5 \pm 3$ ,  $2.5 \pm 0.3$  and  $4.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Welz et al., 2014; Chung et al., 2019; Sipilä et al., 2014).

**Table S3** Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of each elementary pathway involved in the initiation reaction of CH<sub>2</sub>OO with HCOOH computed at different temperatures

T/K	$k(\text{TS}_{\text{ent}1})$	$k(\text{TS}_{\text{ent}2})$	$k(\text{TS}_{\text{ent}3})$	$k(\text{TS}_{\text{ent}4})$	$k_{\text{tot-CH}_2\text{OO}}$
273	$1.7 \times 10^{-10}$	$3.6 \times 10^{-12}$	$1.0 \times 10^{-22}$	$3.6 \times 10^{-12}$	$1.8 \times 10^{-10}$
280	$1.6 \times 10^{-10}$	$2.9 \times 10^{-12}$	$1.2 \times 10^{-22}$	$3.1 \times 10^{-12}$	$1.7 \times 10^{-10}$
298	$1.4 \times 10^{-10}$	$1.9 \times 10^{-12}$	$2.2 \times 10^{-22}$	$2.3 \times 10^{-12}$	$1.4 \times 10^{-10}$
300	$1.4 \times 10^{-10}$	$1.8 \times 10^{-12}$	$2.4 \times 10^{-22}$	$2.2 \times 10^{-12}$	$1.4 \times 10^{-10}$
320	$1.3 \times 10^{-10}$	$1.2 \times 10^{-12}$	$4.9 \times 10^{-22}$	$1.6 \times 10^{-12}$	$1.3 \times 10^{-10}$

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

**Table S4** Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of each elementary pathway involved in the initiation reaction of *anti*-CH<sub>3</sub>CHOO with HCOOH computed at different temperatures

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

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

**Table S5** Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of each elementary pathway involved in the initiation reaction of *syn*-CH<sub>3</sub>CHOO with HCOOH computed at different temperatures

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

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

**Table S6** Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of each elementary pathway involved in the initiation reaction of  $(\text{CH}_3)_2\text{OO}$  with  $\text{HCOOH}$  computed at different temperatures

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

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

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  $5.0 \times 10^{10}$  molecules  $\text{cm}^{-3}$  in the simulation, which is taken from the typical concentration of HCOOH in the tropical forest environments (Vereecken et al., 2012).  $\text{N}_2$  is applied as the buffer gas. A single exponential down model is employed to simulate the collision transfer ( $\langle \Delta E \rangle_{\text{down}} = 200 \text{ cm}^{-1}$ ). 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 KiSTheP 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  $k_{\text{tot-CH}_2\text{OO}}$  of  $\text{CH}_2\text{OO}$  reaction with HCOOH are in excess of  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and they exhibit a slightly negative temperature dependence in the temperature range studied.  $k_{\text{tot-CH}_2\text{OO}}$  is estimated to be  $1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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) ( $[1.0 \pm 0.03] \times 10^{-10}$ ).  $k(\text{TS}_{\text{ent}1})$  is approximately equal to  $k_{\text{tot-CH}_2\text{OO}}$  in the whole temperature range, and it decreases in the range of  $1.7 \times 10^{-10}$  (273 K) to  $1.2 \times 10^{-10}$  (400 K)  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with increasing temperature.  $k(\text{TS}_{\text{ent}1})$  is several orders of magnitude greater than  $k(\text{TS}_{\text{ent}2})$ ,  $k(\text{TS}_{\text{ent}3})$  and  $k(\text{TS}_{\text{ent}4})$  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  $\text{CH}_2\text{OO}$  reaction with  $\text{HCOOH}$ , the rate coefficient of each elementary pathway involved in the  $\text{anti-CH}_3\text{CHOO} + \text{HCOOH}$  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  $\text{syn-CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  with  $\text{HCOOH}$  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  $\text{syn-CH}_3\text{CHOO} + \text{HCOOH}$  and  $(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  systems. At ambient temperature, the total rate coefficients of  $\text{HCOOH}$  reactions with  $\text{anti-CH}_3\text{CHOO}$ ,  $\text{syn-CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  are estimated to be 5.9, 2.7 and  $4.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, which are consistent with the prior experimental measurements of  $5 \pm 3$ ,  $2.5 \pm 0.3$  and  $4.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (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  $\text{HCOOH}$  is assessed by the reaction enthalpy ( $\Delta H$ ), which is defined as the difference between the enthalpies of formation ( $\Delta_f H$ ) of the products and reactants ( $\Delta_f H$ ). 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  $\text{CH}_2\text{OO}$ . 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  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  are available ( $\Delta_f H(\text{H}_2) = 0.00 \text{ kcal}\cdot\text{mol}^{-1}$ ;  $\Delta_f H(\text{CH}_4) = -17.82 \text{ kcal}\cdot\text{mol}^{-1}$ ;  $\Delta_f H(\text{H}_2\text{O}) = -57.79 \text{ kcal}\cdot\text{mol}^{-1}$ ).

(4)

As seen in Table S2, the enthalpy of formation of  $\text{CH}_2\text{OO}$  is calculated to be  $23.23 \text{ kcal}\cdot\text{mol}^{-1}$ , 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  $\text{anti-CH}_3\text{CHOO}$  decreases by  $12.95 \text{ kcal}\cdot\text{mol}^{-1}$  compared to the enthalpy of formation of  $\text{CH}_2\text{OO}$ , and the enthalpy of formation of Pent1b decreases by  $12.12 \text{ kcal}\cdot\text{mol}^{-1}$  compared to the enthalpy of formation of Pent1a. The reaction enthalpies decrease in the order of  $-44.69 \text{ kcal}\cdot\text{mol}^{-1}$  ( $\text{CH}_2\text{OO} + \text{HCOOH} \rightarrow \text{Pent1a}$ )  $< -43.86 \text{ kcal}\cdot\text{mol}^{-1}$  ( $\text{anti-CH}_3\text{CHOO} + \text{HCOOH} \rightarrow \text{Pent1b}$ )  $< -38.13 \text{ kcal}\cdot\text{mol}^{-1}$  ( $\text{syn-CH}_3\text{CHOO} + \text{HCOOH} \rightarrow \text{Pent1c}$ )  $< -37.12 \text{ kcal}\cdot\text{mol}^{-1}$  ( $(\text{CH}_3)_2\text{COO} + \text{HCOOH} \rightarrow \text{Pent1d}$ ), 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 ( $\Delta_f H$ ) 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 <sup>-1</sup> )	Refs. (kcal·mol <sup>-1</sup> )
CH <sub>2</sub> OO	23.23	22.92 <sup>a</sup>
		24.59 <sup>b</sup>
<i>anti</i> -CH <sub>3</sub> OO	10.28	
<i>syn</i> -CH <sub>3</sub> CHOO	6.73	
(CH <sub>3</sub> ) <sub>2</sub> COO	-6.77	
HCOOH		-90.62 (exp)
HC(O)OCH <sub>2</sub> OOH (Pent1a)	-112.08	
HC(O)OCH(CH <sub>3</sub> )OOH (Pent1b)	-124.20	
HC(O)OCH(CH <sub>3</sub> )OOH (Pent1c)	-122.02	
HC(O)OC(CH <sub>3</sub> ) <sub>2</sub> OOH (Pent1d)	-134.51	

Exp is taken from NIST Chemistry Webbook

<sup>a</sup> the value is obtained at the G4 level of theory (Chen et al., 2016)

<sup>b</sup> 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 ( $\Delta H$ ), which is defined as the difference between the enthalpies of formation ( $\Delta H_f^\circ$ ) of the products and reactants ( $\Delta H_f^\circ$ ). 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  $\text{CH}_2\text{OO}$ . 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  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  are available ( $\Delta H_f^\circ(\text{H}_2) = 0.00 \text{ kcal}\cdot\text{mol}^{-1}$ ;  $\Delta H_f^\circ(\text{CH}_4) = -17.82 \text{ kcal}\cdot\text{mol}^{-1}$ ;  $\Delta H_f^\circ(\text{H}_2\text{O}) = -57.79 \text{ kcal}\cdot\text{mol}^{-1}$ ).*

(4)

*As seen in Table S2, the enthalpy of formation of  $\text{CH}_2\text{OO}$  is calculated to be  $23.23 \text{ kcal}\cdot\text{mol}^{-1}$ , 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- $\text{CH}_3\text{CHOO}$  decreases by  $12.95 \text{ kcal}\cdot\text{mol}^{-1}$  compared to the enthalpy of formation of  $\text{CH}_2\text{OO}$ , and the enthalpy of formation of Pent1b decreases by  $12.12 \text{ kcal}\cdot\text{mol}^{-1}$  compared to the enthalpy of formation of Pent1a. The reaction enthalpies decrease in the order of  $-44.69$  ( $\text{CH}_2\text{OO} + \text{HCOOH} \rightarrow \text{Pent1a}$ )  $< -43.86$  (anti- $\text{CH}_3\text{CHOO} + \text{HCOOH} \rightarrow \text{Pent1b}$ )  $< -38.13$  (syn- $\text{CH}_3\text{CHOO} + \text{HCOOH} \rightarrow \text{Pent1c}$ )  $< -37.12 \text{ kcal}\cdot\text{mol}^{-1}$  ( $(\text{CH}_3)_2\text{COO} + \text{HCOOH} \rightarrow \text{Pent1d}$ ), 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 confirmed 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  $\text{H}_2\text{O}$ , HCOOH,  $\text{SO}_2$  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  $-\text{CH}_3$  group relative to the terminal oxygen of MVK-OO, whereas *cis* and *trans* refer to the orientation of the  $\text{C}_8=\text{C}_9$  bond relative to the  $\text{C}_1=\text{O}_2$  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<sup>-1</sup>, 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<sub>2</sub>O 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.  $k_{\text{eff}}(\text{MVK-OO}+\text{H}_2\text{O})$  is nearly identical to  $k_{\text{eff}}(\text{MVK-OO}+\text{HCOOH})$ , which is greater than  $k_{\text{eff}}(\text{MVK-OO}+\text{SO}_2)$  and  $k_{\text{eff}}(\text{MVK-OO}+\text{HPMF})$  when the concentration of HPMF is the same as that of HCOOH.  $k_{\text{eff}}(\text{MVK-OO}+\text{H}_2\text{O})$  and  $k_{\text{eff}}(\text{MVK-OO}+\text{HCOOH})$  are greater than  $k_{\text{eff}}(\text{MVK-OO}+\text{SO}_2)$ , which, in turn, are greater than  $k_{\text{eff}}(\text{MVK-OO}+\text{HPMF})$  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<sup>-1</sup>) 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<sub>2</sub>O, HCOOH, SO<sub>2</sub>, 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<sup>-1</sup>, 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<sub>2</sub>O 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.  $k_{\text{eff}(\text{MVK-OO}+\text{H}_2\text{O})}$  is nearly identical to  $k_{\text{eff}(\text{MVK-OO}+\text{HCOOH})}$ , which is greater than  $k_{\text{eff}(\text{MVK-OO}+\text{SO}_2)}$  and  $k_{\text{eff}(\text{MVK-OO}+\text{HPMF})}$  when the concentration of HPMF is the same as that of HCOOH.  $k_{\text{eff}(\text{MVK-OO}+\text{H}_2\text{O})}$  and  $k_{\text{eff}(\text{MVK-OO}+\text{HCOOH})}$  are greater than  $k_{\text{eff}(\text{MVK-OO}+\text{SO}_2)}$ , which, in turn, are greater than  $k_{\text{eff}(\text{MVK-OO}+\text{HPMF})}$  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<sub>2</sub>O, HCOOH and SO<sub>2</sub>), 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 ( $k_{\text{eff}} = k[\text{coreactant}]$ ) for distinct SCI reactions with H<sub>2</sub>O, HCOOH, SO<sub>2</sub> 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<sub>2</sub>O, HCOOH and SO<sub>2</sub> 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<sup>-3</sup>, respectively (Vereecken, 2012). For the reactions of CH<sub>2</sub>OO with H<sub>2</sub>O, HCOOH, and SO<sub>2</sub>, 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<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively (Welz et al., 2012 and 2014; Chao et al., 2015), which translate into  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{H}_2\text{O})}$ ,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HCOOH})}$  and  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{SO}_2)}$  of  $5.9\text{-}9.2 \times 10^2$ ,  $5.5\text{-}11$ , and  $0.7\text{-}3.5$  s<sup>-1</sup>, respectively. The result reveals that the reaction of CH<sub>2</sub>OO with H<sub>2</sub>O is the most important bimolecular reaction.  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HCOOH})}$  is greater by a factor of 3-8 than  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{SO}_2)}$ , indicating that the reaction of CH<sub>2</sub>OO with HCOOH is favored over reaction with SO<sub>2</sub>. Similar conclusion is also obtained from the results of  $k_{\text{eff}}$  for the reactions of *anti*-CH<sub>3</sub>CHOO, *syn*-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO with H<sub>2</sub>O, HCOOH and SO<sub>2</sub> that SCIs reactions with H<sub>2</sub>O are faster than with HCOOH, which, in turn, are faster than with SO<sub>2</sub>.

According to the results shown in the Table 2, the room temperature rate coefficient for the reaction of CH<sub>2</sub>OO with HPMF is calculated to be  $2.7 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

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,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HPMF})}$  is estimated to be  $1.4\text{-}2.7 \text{ s}^{-1}$ , which is significantly lower than  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{H}_2\text{O})}$  and  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HCOOH})}$ .  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HPMF})}$  is nearly identical to  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{SO}_2)}$ , indicating that the  $\text{CH}_2\text{OO} + \text{HPMF}$  reaction is competitive with the  $\text{CH}_2\text{OO} + \text{SO}_2$  system. Previous model-measurement studies have estimated the surface-level SCIs concentrations in the range of  $1.0 \times 10^4$  to  $1.0 \times 10^5 \text{ molecules cm}^{-3}$  (Khan et al., 2018; Novelli et al., 2017). If we assume that the concentration of HPMF is equal to that of SCIs,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HPMF})}$  is calculated to be  $2.7\text{-}27 \times 10^{-7} \text{ s}^{-1}$ , which is several orders of magnitude lower than  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{H}_2\text{O})}$ ,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HCOOH})}$  and  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{SO}_2)}$ . This result indicates that the reaction of  $\text{CH}_2\text{OO}$  with HPMF is of less importance. Similar conclusion is also obtained from the reactions of *anti*- $\text{CH}_3\text{CHOO}$ , *syn*- $\text{CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  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 ( $k_{\text{eff}} = k[\text{coreactant}]$ ) for distinct SCI reactions with HPMF,  $\text{H}_2\text{O}$ , HCOOH and  $\text{SO}_2$  at the tropical forest environments

SCIs	Coreactant	[Coreactant]	$k$	$k_{\text{eff}}$	Reference
		(molecules $\text{cm}^{-3}$ )	( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	( $\text{s}^{-1}$ )	
$\text{CH}_2\text{OO}$	$\text{H}_2\text{O}$	$3.9\text{-}6.1 \times 10^{17}$	$< 1.5 \times 10^{-15}$	$5.9\text{-}9.2 \times 10^2$	Chao et al., (2015)
HCOOH	$5.0\text{-}10.0 \times 10^{10}$	$[1.1 \pm 0.1] \times 10^{-10}$	$5.5\text{-}11$		Welz et al., (2014)
$\text{SO}_2$	$1.7\text{-}9.0 \times 10^{10}$	$[3.9 \pm 0.7] \times 10^{-11}$	$0.7\text{-}3.5$		Welz et al., (2012)
HPMF	-	$2.7 \times 10^{-11}$	-		This work
<i>anti</i> - $\text{CH}_3\text{CHOO}$	$\text{H}_2\text{O}$	$3.9\text{-}6.1 \times 10^{17}$	$[1.0 \pm 0.4] \times$	$3.9\text{-}6.1 \times 10^3$	Taatjes et al.,

$10^{-14}$ 

(2013)

HCOOH	$5.0-10.0 \times 10^{10}$	$[5 \pm 3] \times 10^{-10}$	25.0-50.0	Welz et al., (2014)
SO <sub>2</sub>	$1.7-9.0 \times 10^{10}$	$[6.7 \pm 1.0] \times 10^{-11}$	1.1-6.0	Taatjes et al., (2013)
HPMF	-	$3.3 \times 10^{-10}$	-	This work
<i>syn</i> -CH <sub>3</sub> CHOO	H <sub>2</sub> O	$3.9-6.1 \times 10^{17}$	$< 4.0 \times 10^{-15}$	$1.6-2.4 \times 10^3$ Taatjes et al., (2013)
HCOOH	$5.0-10.0 \times 10^{10}$	$[2.5 \pm 0.3] \times 10^{-10}$	12.5-25.0	Welz et al., (2014)
SO <sub>2</sub>	$1.7-9.0 \times 10^{10}$	$[2.4 \pm 0.3] \times 10^{-11}$	0.4-2.2	Taatjes et al., (2013)
HPMF	-	$1.7 \times 10^{-13}$	-	This work
(CH <sub>3</sub> ) <sub>2</sub> COO	H <sub>2</sub> O	$3.9-6.1 \times 10^{17}$	$< 1.5 \times 10^{-16}$	58.5-91.5 Huang et al., (2015)
HCOOH	$5.0-10.0 \times 10^{10}$	$4.5 \times 10^{-10}$	22.5-45.0	Sipilä et al., (2014)

SO <sub>2</sub>	1.7-9.0 × 10 <sup>10</sup>	1.3 × 10 <sup>-10</sup>	2.2-11.7	Huang et al., (2015)
HPMF	-	2.2 × 10 <sup>-11</sup>	-	This work
<i>syn-trans</i> -MVK-OO	H <sub>2</sub> O	3.9-6.1 × 10 <sup>17</sup>	< 4.0 × 10 <sup>-17</sup>	15.6-24.4 Caravan et al., (2020)
HCOOH	5.0-10.0 × 10 <sup>10</sup>	[3.0 ± 0.1] × 10 <sup>-10</sup>	15.0-30.0	Caravan et al., (2020)
SO <sub>2</sub>	1.7-9.0 × 10 <sup>10</sup>	[4.2 ± 0.6] × 10 <sup>-11</sup>	0.7-3.8	Caravan et al., (2020)
HPMF	-	3.0 × 10 <sup>-11</sup>	-	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<sub>2</sub>O, HCOOH and SO<sub>2</sub>), 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 ( $k_{\text{eff}} = k[\text{coreactant}]$ ) for distinct SCI reactions with H<sub>2</sub>O, HCOOH, SO<sub>2</sub>, 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<sub>2</sub>O, HCOOH and SO<sub>2</sub> in the tropical forest environments are measured to be 3.9-6.1 × 10<sup>17</sup>, 5.0-10 × 10<sup>10</sup>, and 1.7-9.0 × 10<sup>10</sup> molecules cm<sup>-3</sup>, respectively (Vereecken, 2012). For the reactions of CH<sub>2</sub>OO with H<sub>2</sub>O, HCOOH, and SO<sub>2</sub>, the experimental rate coefficients are determined to be < 1.5 × 10<sup>-15</sup>, [1.1 ± 0.1] × 10<sup>-10</sup>, and [3.9 ± 0.7] × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively (Welz et al., 2012 and 2014; Chao et al., 2015), which translate into  $k_{\text{eff(CH}_2\text{OO+H}_2\text{O)}}$ ,  $k_{\text{eff(CH}_2\text{OO+HCOOH)}}$  and  $k_{\text{eff(CH}_2\text{OO+SO}_2)}$  of 5.9-9.2 × 10<sup>2</sup>, 5.5-11, and 0.7-3.5 s<sup>-1</sup>, respectively. The result reveals that the reaction of CH<sub>2</sub>OO with H<sub>2</sub>O is the most important bimolecular reaction.  $k_{\text{eff(CH}_2\text{OO+HCOOH)}}$  is greater by a factor of 3-8 than  $k_{\text{eff(CH}_2\text{OO+SO}_2)}$ , indicating that the reaction of CH<sub>2</sub>OO with HCOOH is favored over reaction with SO<sub>2</sub>. Similar conclusion is also obtained from the results of  $k_{\text{eff}}$  for the reactions of anti-CH<sub>3</sub>CHOO, *syn*-CH<sub>3</sub>CHOO and*

$(\text{CH}_3)_2\text{COO}$  with  $\text{H}_2\text{O}$ ,  $\text{HCOOH}$  and  $\text{SO}_2$  that SCIs reactions with  $\text{H}_2\text{O}$  are faster than with  $\text{HCOOH}$ , which, in turn, are faster than with  $\text{SO}_2$ .

According to the results shown in the Table 2, the room temperature rate coefficient for the reaction of  $\text{CH}_2\text{OO}$  with HPMF is calculated to be  $2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . 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  $\text{HCOOH}$ ,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HPMF})}$  is estimated to be  $1.4\text{-}2.7 \text{ s}^{-1}$ , which is significantly lower than  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{H}_2\text{O})}$  and  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HCOOH})}$ .  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HPMF})}$  is nearly identical to  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{SO}_2)}$ , indicating that the  $\text{CH}_2\text{OO} + \text{HPMF}$  reaction is competitive with the  $\text{CH}_2\text{OO} + \text{SO}_2$  system. Previous model-measurement studies have estimated the surface-level SCIs concentrations in the range of  $1.0 \times 10^4$  to  $1.0 \times 10^5 \text{ molecules cm}^{-3}$  (Khan et al., 2018; Novelli et al., 2017). If we assume that the concentration of HPMF is equal to that of SCIs,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HPMF})}$  is calculated to be  $2.7\text{-}27 \times 10^{-7} \text{ s}^{-1}$ , which is several orders of magnitude lower than  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{H}_2\text{O})}$ ,  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{HCOOH})}$  and  $k_{\text{eff}(\text{CH}_2\text{OO}+\text{SO}_2)}$ . This result indicates that the reaction of  $\text{CH}_2\text{OO}$  with HPMF is of less importance. Similar conclusion is also obtained from the reactions of *anti*- $\text{CH}_3\text{CHOO}$ , *syn*- $\text{CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  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  $\text{CH}_2\text{OO}$  with  $\text{HCOOH}$  increases first and then decreases with increasing the number of  $\text{CH}_2\text{OO}$ . The  $P^0$  of the adduct product  $\text{HC}(\text{O})\text{O}(\text{CH}_2\text{OO})_3\text{H}$  is maximum when the number of  $\text{CH}_2\text{OO}$  is equal to three. The  $P^0$  of adduct products included in the successive reactions of *anti*- $\text{CH}_3\text{CHOO}$  with  $\text{HCOOH}$  decreases significantly as the number of *anti*- $\text{CH}_3\text{CHOO}$  is increased. Similar phenomenon is also observed from the successive reactions of *syn*- $\text{CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  with  $\text{HCOOH}$ . Notably, the  $P^0$  of adduct products decreases obviously when the size of SCIs increases. For example, the  $P^0$  of the adduct product  $\text{HC}(\text{O})\text{O}(\text{CH}_2\text{OO})_3\text{H}$  in the  $n\text{CH}_2\text{OO} + \text{HCOOH}$  reaction is estimated to be  $4.43 \times 10^{-3} \text{ atm}$ , which is greater than those of the corresponding adduct products in the *nanti*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  ( $7.12 \times 10^{-4}$ ), *nsyn*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  ( $7.12 \times 10^{-4}$ ), and  $n(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  ( $1.27 \times 10^{-4}$ ) 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  $n\text{CH}_2\text{OO} + \text{HCOOH}$  reaction decreases with increasing the number of  $\text{CH}_2\text{OO}$ . According to the Volatility Basis Set (VBS) of organic compounds (Donahue et al., 2012), these adduct products belong to volatile organic compounds (VOC,  $c^0 > 3 \times 10^6 \text{ ug/m}^3$ ). Similarly, the  $c^0$  of adduct products included in the *nanti*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$ , *nsyn*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$ , and  $n(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  reactions decreases when the number of SCIs increases. It deserves mentioning that the adduct products in the *nanti*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  and *nsyn*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  reactions belong to intermediate volatility organic compounds (IVOC,  $300 < c^0 < 3 \times 10^6 \text{ ug/m}^3$ ) when the number of SCIs is equal to five. However, the adduct products in the  $n(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  reaction become IVOC when the number of  $(\text{CH}_3)_2\text{COO}$  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)	$c^0$ ( $\text{ug/m}^3$ )
$n \text{ CH}_2\text{OO} + \text{HCOOH}$			
$n = 1$	$\text{HC(O)OCH}_2\text{OOH}$	$2.12 \times 10^{-3}$	$7.86 \times 10^7$
$n = 2$	$\text{HC(O)O(CH}_2\text{OO)}_2\text{H}$	$3.80 \times 10^{-3}$	$3.99 \times 10^7$
$n = 3$	$\text{HC(O)O(CH}_2\text{OO)}_3\text{H}$	$4.43 \times 10^{-3}$	$3.91 \times 10^7$
$n = 4$	$\text{HC(O)O(CH}_2\text{OO)}_4\text{H}$	$4.21 \times 10^{-3}$	$3.29 \times 10^7$
$n = 5$	$\text{HC(O)O(CH}_2\text{OO)}_5\text{H}$	$3.59 \times 10^{-3}$	$2.12 \times 10^7$

n *anti*-CH<sub>3</sub>CHOO +  
HCOOH

n = 1	HC(O)OCH(CH <sub>3</sub> )OOH	$1.25 \times 10^{-3}$	$8.32 \times 10^6$
n = 2	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>2</sub> H	$1.13 \times 10^{-3}$	$7.57 \times 10^6$
n = 3	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>3</sub> H	$7.12 \times 10^{-4}$	$6.49 \times 10^6$
n = 4	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>4</sub> H	$3.90 \times 10^{-4}$	$4.50 \times 10^6$
n = 5	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>5</sub> H	$2.01 \times 10^{-4}$	$2.81 \times 10^6$

n *syn*-CH<sub>3</sub>CHOO +  
HCOOH

n = 1	HC(O)OCH(CH <sub>3</sub> )OOH	$1.25 \times 10^{-3}$	$8.32 \times 10^6$
n = 2	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>2</sub> H	$1.13 \times 10^{-3}$	$7.57 \times 10^6$
n = 3	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>3</sub> H	$7.12 \times 10^{-4}$	$6.49 \times 10^6$

n = 4	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>4</sub> H	$3.90 \times 10^{-4}$	$4.50 \times 10^6$
n = 5	HC(O) O(CH(CH <sub>3</sub> )OO) <sub>5</sub> H	$2.01 \times 10^{-4}$	$2.81 \times 10^6$
n (CH <sub>3</sub> ) <sub>2</sub> COO + HCOOH			
n = 1	HC(O)OC(CH <sub>3</sub> ) <sub>2</sub> OOH	$7.23 \times 10^{-4}$	$3.50 \times 10^6$
n = 2	HC(O)O( C(CH <sub>3</sub> ) <sub>2</sub> OO) <sub>2</sub> H	$3.50 \times 10^{-4}$	$2.74 \times 10^6$
n = 3	HC(O)O( C(CH <sub>3</sub> ) <sub>2</sub> OO) <sub>3</sub> H	$1.27 \times 10^{-4}$	$1.38 \times 10^6$
n = 4	HC(O)O( C(CH <sub>3</sub> ) <sub>2</sub> OO) <sub>4</sub> H	$4.27 \times 10^{-5}$	$5.90 \times 10^5$
n = 5	HC(O)O( C(CH <sub>3</sub> ) <sub>2</sub> OO) <sub>5</sub> H	$1.40 \times 10^{-5}$	$2.36 \times 10^5$

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  $\text{CH}_2\text{OO}$  with  $\text{HCOOH}$  increases first and then decreases with increasing the number of  $\text{CH}_2\text{OO}$ . The  $P^0$  of the adduct product  $\text{HC(O)O(CH}_2\text{OO)}_3\text{H}$  is maximum when the number of  $\text{CH}_2\text{OO}$  is equal to three. The  $P^0$  of adduct products included in the successive reactions of anti- $\text{CH}_3\text{CHOO}$  with  $\text{HCOOH}$  decreases significantly as the number of anti- $\text{CH}_3\text{CHOO}$  is increased. Similar phenomenon is also observed from the successive reactions of syn- $\text{CH}_3\text{CHOO}$  and  $(\text{CH}_3)_2\text{COO}$  with  $\text{HCOOH}$ . Notably, the  $P^0$  of adduct products decreases obviously when the size of SCIs increases. For example, the  $P^0$  of the adduct product  $\text{HC(O)O(CH}_2\text{OO)}_3\text{H}$  in the  $n\text{CH}_2\text{OO} + \text{HCOOH}$  reaction is estimated to be  $4.43 \times 10^{-3}$  atm, which is greater than those of the corresponding adduct products in the nanti- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  ( $7.12 \times 10^{-4}$ ), nsyn- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  ( $7.12 \times 10^{-4}$ ), and  $n(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  ( $1.27 \times 10^{-4}$ ) 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  $\text{HCOOH}$  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  $n\text{CH}_2\text{OO} + \text{HCOOH}$  reaction decreases with increasing the number of  $\text{CH}_2\text{OO}$ . 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<sup>3</sup>). Similarly, the  $c^0$  of adduct products included in the nanti- $\text{CH}_3\text{CHOO} + \text{HCOOH}$ , nsyn- $\text{CH}_3\text{CHOO} + \text{HCOOH}$ , and  $n(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  reactions decreases when the number of SCIs increases. It deserves mentioning that the adduct products in the nanti- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  and nsyn- $\text{CH}_3\text{CHOO} + \text{HCOOH}$  reactions belong to intermediate volatility organic compounds (IVOC,  $300 < c^0 < 3 \times 10^6$  ug/m<sup>3</sup>) when the number of SCIs is equal to five. However, the adduct products in the  $n(\text{CH}_3)_2\text{COO} + \text{HCOOH}$  reaction become IVOC when the number of  $(\text{CH}_3)_2\text{COO}$  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  $\text{HCOOH}$ .

- 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.

## References

Barber, V. P., Pandit, S., Green, A. M., Trongsirawat, N., Walsh, P. J., Klippenstein, S. J., and Lester, M. I.: Four-carbon Criegee intermediate from isoprene ozonolysis: methyl vinyl ketone oxide synthesis, infrared spectrum, and OH production, *J. Am. Chem. Soc.*, 140, 10866-10880, <https://doi.org/10.1021/jacs.8b06010>, 2018.

Barley, M. H., and McFiggans, G.: The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol, *Atmos. Chem. Phys.*, 10, 749-767, <https://doi.org/10.5194/acp-10-749-2010>, 2010.

Canneaux, S., Bohr, F., and Henon, E.: KiSTheIP: a program to predict thermodynamic properties and rate constants from quantum chemistry results, *J. Comput. Chem.*, 35, 82-93, <https://doi.org/10.1002/jcc.23470>, 2013.

Caravan, R. L., Vansco, M. F., Au, K., Khan, M. A. H., Li, Y. L., Winiberg, F. A. F., Zuraski, K., Lin, Y. H., Chao, W., Trongsirawat, N., Walsh, P. J., Osborn, D. L., Percival, C. J., Lin, J. J. M., Shallcross, D. E., Sheps, L., Klippenstein, S. J., Taatjes, C. A., and Lester, M. I.: Direct kinetic measurements and theoretical predictions of an isoprene-derived Criegee intermediate, *Proc. Natl. Acad. Sci. U.S.A.*, 117, 9733-9740, <https://doi.org/10.1073/pnas.1916711117>, 2020.

Chao, W., Hsieh, J. T., Chang, C. H., and Lin, J. J. M.: Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor, *Science*, 347, 751-754, <https://doi.org/10.1126/science.1261549>, 2015.

Chen, L., Wang, W., Wang, W., Liu, Y., Liu, F., Liu, N., and Wang, B.: Water-catalyzed decomposition of the simplest Criegee intermediate CH<sub>2</sub>OO, *Theor. Chem. Acc.*, 135, 131-143, <https://doi.org/10.1007/s00214-016-1894-9>, 2016.

Chung, C. A., Su, J. W., and Lee, Y. P.: Detailed mechanism and kinetics of the reaction of Criegee intermediate CH<sub>2</sub>OO with HCOOH investigated via infrared identification of conformers of hydroperoxymethyl formate and formic acid anhydride, *Phys. Chem. Chem.*

Phys., 21, 21445-21455, <https://doi.org/10.1039/c9cp04168k>, 2019.

Donahue, N. M., Kroll, J. H., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set – Part 2: Diagnostics of organic-aerosol evolution, *Atmos. Chem. Phys.*, 12, 615-634, <https://doi.org/10.5194/acp-12-615-2012>, 2012.

Gilbert, R. G., and Smith, S. C.: *Theory of unimolecular and recombination reactions*; Blackwell Scientific: Carlton, Australia, 1990.

Glowacki, D. R., Liang, C. H., Morley, C., Pilling, M. J., and Robertson, S. H.: MESMER: an open-source master equation solver for multi-energy well reactions, *J. Phys. Chem. A*, 116, 9545-9560, <https://doi.org/10.1021/jp3051033>, 2012.

Huang, H. L., Chao, W., and Lin, J. J. M.: Kinetics of a Criegee intermediate that would survive high humidity and may oxidize atmospheric SO<sub>2</sub>, *Proc. Natl. Acad. Sci. U.S.A.*, 112, 10857-10862, <https://doi.org/10.1073/pnas.1513149112>, 2015.

Kalinowski, J., Räsänen, M., Heinonen, P., Kilpeläinen, I., and Gerber, R. B.: Isomerization and decomposition of a Criegee intermediate in the ozonolysis of alkenes: dynamics using a multireference potential, *Angew. Chem.*, 126, 269-272, <https://doi.org/10.1002/ange.201307286>, 2014.

Karton, A., Kettner, M., and Wild, D. A.: Sneaking up on the Criegee intermediate from below: Predicted photoelectron spectrum of the CH<sub>2</sub>OO<sup>-</sup> anion and W3-F12 electron affinity of CH<sub>2</sub>OO, *Chem. Phys. Lett.*, 585, 15-20, <http://doi.org/10.1016/j.cplett.2013.08.075>, 2013.

Khan, M. A. H., Percival, C. J., Caravan, R. L., Taatjes, C. A., and Shallcross, D. E.: Criegee intermediates and their impacts on the troposphere, *Environ. Sci.: Processes Impacts*, 20, 437-453, <https://doi.org/10.1039/C7EM00585G>, 2018.

Long, B., Bao, J. L., and Truhlar, D. G.: Atmospheric chemistry of Criegee intermediates: unimolecular reactions and reactions with water, *J. Am. Chem. Soc.*, 138, 14409-14422, <https://doi.org/10.1021/jacs.6b08655>, 2016.

Nannoolal, Y., Rarey, J., and Ramjugernatha, D.: Estimation of pure component properties Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, *Fluid Phase Equilibria*, 269, 117-133, <https://doi.org/10.1016/j.fluid.2008.04.020>, 2008.

Nannoolal, Y., Rarey, J., Ramjugernatha, D., and Cordes, W.: Estimation of pure component properties Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via group contributions and group interactions, *Fluid Phase Equilibria*, 226, 45-63, <https://doi.org/10.1016/j.fluid.2004.09.001>, 2004.

Novelli, A., Hens, K., Ernest, C. T., Martinez, M., Nölscher, A. C., Sinha, V., Paasonen, P., Petäjä, T., Sipilä, M., Elste, T., Plass-Dülmer, C., Phillips, G. J., Kubistin, D., Williams, J., Vereecken, L., Lelieveld, J., and Harder, H.: Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument, *Atmos. Chem. Phys.*, 17, 7807-7826, <https://doi.org/10.5194/acp-17-7807-2017>, 2017.

O'Meara, S., Booth, A. M., Barley, M. H., Topping, D., and McFiggans, G.: An assessment of vapour pressure estimation methods, *Phys. Chem. Chem. Phys.*, 16, 19453-19469, <https://doi.org/10.1039/C4CP00857J>, 2014.

Pankow, J. F., and Asher, W. E.: SIMPOL.1: a simple group contribution method for

predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, *Atmos. Chem. Phys.*, 8, 2773-2796, <https://doi.org/10.5194/acp-8-2773-2008>, 2008.

Peltola, J., Seal, P., Inkilä, A., and Eskola, A.: Time-resolved, broadband UV-absorption spectrometry measurements of Criegee intermediate kinetics using a new photolytic precursor: unimolecular decomposition of CH<sub>2</sub>OO and its reaction with formic acid, *Phys. Chem. Chem. Phys.*, 22, 11797-11808, <https://doi.org/10.1039/d0cp00302f>, 2020.

Raghunath, P., Lee, Y. P., and Lin, M. C.: Computational chemical kinetics for the reaction of Criegee intermediate CH<sub>2</sub>OO with HNO<sub>3</sub> and its catalytic conversion to OH and HCO, *J. Phys. Chem. A*, 121, 3871-3878, <https://doi.org/10.1021/acs.jpca.7b02196>, 2017.

Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin Iii, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V. M., and Petäjä, T.: Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO<sub>2</sub> and organic acids, *Atmos. Chem. Phys.*, 14, 12143-12153, <https://doi.org/10.5194/acp-14-12143-2014>, 2014.

Taatjes, C. A., Welz, O., Eskola, A. J., Savee, J. D., Scheer, A. M., Shallcross, D. E., Rotavera, B., Lee, E. P. F., Dyke, J. M., Mok, D. K. W., Osborn, D. L., and Percival, C. J.: Direct measurements of conformer-dependent reactivity of the Criegee intermediate CH<sub>3</sub>CHOO, *Science*, 340, 177-180, <https://doi.org/10.1126/science.1234689>, 2013.

Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO<sub>2</sub>, and SO<sub>2</sub>, and their fate in the atmosphere, *Phys. Chem. Chem. Phys.*, 14, 14682-14695, <https://doi.org/10.1039/c2cp42300f>, 2012.

Welz, O., Eskola, A. J., Sheps, L., Rotavera, B., Savee, J. D., Scheer, A. M., Osborn, D. L., Lowe, D., Booth, A. M., Xiao, P., Khan, M. A. H., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Rate coefficients of C(1) and C(2) Criegee intermediate reactions with formic and acetic Acid near the collision limit: direct kinetics measurements and atmospheric implications, *Angew. Chem. Int. Ed.*, 53, 4547-4550, <https://doi.org/10.1002/anie.201400964>, 2014.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct kinetic measurements of Criegee intermediate (CH<sub>2</sub>OO) formed by reaction of CH<sub>2</sub>I with O<sub>2</sub>, *Science*, 335, 204-207, <https://doi.org/10.1126/science.1213229>, 2012.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2022-376/acp-2022-376-AC1-supplement.pdf>