

Interactive comment on “Oligomerization Reactions of Criegee Intermediates with Hydroxyalkyl Hydroperoxides: Mechanism, Kinetics, and Structure-Reactivity Relationship” by Long Chen et al.

Long Chen et al.

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Prof. Yu Huang Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, 710061, China Tel./Fax: (86) 29-62336261 E-mail: huangyu@ieecas.cn Jan. 31, 2019 Dear reviewer, Revision for Manuscript acp-2018-935 We thank you very much for giving us the opportunity to revise our manuscript. We highly appreciate the reviewer for their comments and suggestions on the manuscript entitled “Mechanistic and Kinetics Investigations of Oligomer Formation from Criegee Intermediates Reactions with Hydroxyalkyl Hydroperoxides”. We

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have made revisions of our manuscript carefully according to the comments and suggestions of reviewer. The revised contents are marked in blue color. The response letter to reviewers is attached at the end of this cover letter. We hope that the revised manuscript can meet the requirement of Atmospheric Chemistry & Physics. Any further modifications or revisions, please do not hesitate to contact us. Look forward to hearing from you as soon as possible.

Best regards, Yu Huang

Comments of reviewer #2

1. First of all, I think that the title of this study goes too far. The main focus of this study refers just to the reaction of Carbonyl oxides with HHPs, although a second step, namely the mechanisms for the interaction of the products of these reaction with Carbonyl oxides is taken into account. Response: The title of this study has been revised to “Mechanistic and Kinetics Investigations of Oligomer formation from Criegee Intermediates Reactions with Hydroxyalkyl Hydroperoxides”.

2. Along the text, the authors refer to several reaction products, as for instance, P2c, P2b and so on, but the structure of these compounds is not mentioned, which makes the work difficult to follow. Response: Based on the Reviewer’s suggestion, the structures of all reactants and products are added in the revised manuscript and supplement figures.

Figure 2. PES (ΔG and ΔE (italic)) for the reaction of CH_2OO with $\text{HO-CH}_2\text{OO-H}$ (Pa1) computed at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory

Figure 3. PES (ΔG and ΔE (italic)) for the reactions of $\text{HO-C(CH}_3\text{)HOO-H}$ with anti-(a) and syn- CH_3CHOO (b) calculated at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory

Figure 4. PES (ΔG and ΔE (italic)) for the reaction of $(\text{CH}_3)_2\text{COO}$ with $\text{HO-C(CH}_3\text{)}_2\text{OO-H}$ (Pa3) calculated at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory

Figure 5. PES (ΔG and ΔE (italic)) of distinct SCI reactions with $\text{HO-CH}_2\text{OO-H}$ (Pa1) calculated at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory

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3. Some important references misses, as for instance CPL, 2001,337, 199, JPCA, 2001,105,446, JACS, 1997, 119, 330, CPC 2002, 2, 215, JPCA, 2003, 107, 5812, J. Atmos. Chem, 2000, 35, 165 and references therein. Response: The references on the unimolecular decay of HHPs generated from isoprene ozonolysis, and OH radicals production from alkene ozonolysis are added in the Introduction of the revised manuscript. Thanks for suggesting these closely related references, which have now been cited in the revised manuscript. The corresponding sentences have been added in the page 4 line 90-92, page 6 line 145-148 and page 3 line 57-61 of the revised manuscript in blue color: Winterhalter et al. (2001) studied the mechanism and products of gas phase ozonolysis of β -pinene, and found that the main products are the excited C9-Cl plus HCHO. Aplincourt et al. (2003) investigated the unimolecular decay and water-catalyzed decomposition of HHPs generated from isoprene ozonolysis, and found that the main products are methyl vinyl ketone (MVK) or methacroleine (MAC) plus H₂O₂. The thermal unimolecular decay of vibrationally excited Cls is thought to be an important nonphotolytic source of atmospheric hydroxyl (OH) radicals, particularly in low light conditions, urban environments, and heavily forested areas (Lester et al., 2018; Foreman et al., 2016; Kidwell et al., 2016; Green et al., 2017; Zhang et al., 2002; Cremer et al., 2001; Anglada et al., 2002). 4. Regarding the theoretical approach, the authors state that all stationary points have been computing using the M06-2X functional, and for some selected elementary reactions they have performed single point energy calculations at CCSD(T) level of theory, pointing out that the deviations in the free energy barriers computed with both approaches range between 1.5-1.6 kcal/mol. The authors should clarify in which cases they have computed the energy barriers using both approaches, if they have taken into account basis set superposition corrections. They should compare the results of both approaches, for instance with results from the literature involving the reaction with water vapor (section 3.1) with results from the literature, where energy barriers are reported at CCSD(T)/CBS level of theory. Response: In the present study, the geometries of all stationary points on PES are optimized at the M06-2X/6-311+G(2df,2p) level of theory. For improved energies, single point calculations at

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the M06-2X/def2-TZVP level are performed. In order to evaluate the reliability of M06-2X functional in computing energies, the single point energies of species involved in the some selected elementary reactions (R1a-R1d, R3a-R3d and R5a-R5d) are recalculated at the CCSD(T)/6-311+G(2df,2p) level based on the M06-2X/6-311+G(2df,2p) optimized geometries. Furthermore, the basis set superposition error (BSSE) is performed using the counterpoise method proposed by Boys and Bernardi (Boys et al., 1970). The electronic-energy ($\Delta E_{a\#}$) and free-energy ($\Delta G_{a\#}$) barriers comparisons of both approaches for considering BSSE correction and not considering are listed in Table S1. As shown in Table S1, the BSSE correction contributes to the barriers ~ 1.4 (CCSD(T)) and ~ 0.4 (M06-2X) kcal mol^{-1} , respectively. The mean absolute deviations (MAD) of both approaches are 0.98 ($\Delta E_{a\#}$) and 0.96 ($\Delta G_{a\#}$) kcal mol^{-1} when without considering BSSE correction, while they are 0.38 ($\Delta E_{a\#}$) and 0.34 ($\Delta G_{a\#}$) kcal mol^{-1} when considering BSSE correction. The result shows that the M06-2X method in combination with the BSSE correction afford energies similar to those determined by the accurate and well recognized CCSD(T) level calculation. Considering the computational costs, the M06-2X/def2-TZVP method is selected to perform the single-point energy calculation for the title reaction system. For the bimolecular reaction of carbonyl oxide with water dimer, the barriers ($\Delta E_{a\#}$ and $\Delta G_{a\#}$) are calculated using the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) method, and compared to the literature results. As shown in Table 1, the barrier differences between the computational and literature ones that were derived from the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(2df,2p) method (Anglada et al., 2016) are 0.5-1.0 kcal mol $^{-1}$. Such discrepancies may be attributed to the different theoretical methods used in computing energies. The barrier of Entry 4 is 3.3 kcal mol $^{-1}$, which is lower than the corresponding CCSD(T)/CBS result by 0.5 kcal mol $^{-1}$ (Anglada et al., 2016). The results show that the M06-2X method provides energies similar to those determined by the CCSD(T) level calculation. Corresponding descriptions have been added in the page 8 line 198-215 and page 10 line 264-271 of the revised manuscript: In order to obtain a better evaluation on the reliability of M06-2X functional in computing energies, the single point

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energies of species included in some selected elementary reactions (R1a-R1d, R3a-R3d and R5a-R5d) are recalculated at the CCSD(T)/6-311+G(2df,2p) level based on the M06-2X/6-311+G(2df,2p) optimized geometries. Furthermore, the basis set superposition error (BSSE) is performed using the counterpoise method described by Boys and Bernardi (1970) to estimate the stability of the pre-reactive complexes. The electronic-energy ($\Delta E_{\text{a\#}}$) and free-energy ($\Delta G_{\text{a\#}}$) barriers comparisons of both approaches for considering BSSE correction and not considering are listed in Table S1. As shown in Table S1, the contributions of BSSE corrections to the barriers are ~ 1.4 (CCSD(T)) and ~ 0.4 (M06-2X) kcal mol⁻¹, respectively. The mean absolute deviations (MAD) of both approaches are 0.98 ($\Delta E_{\text{a\#}}$) and 0.96 ($\Delta G_{\text{a\#}}$) kcal mol⁻¹ when without considering BSSE correction, while they become 0.38 ($\Delta E_{\text{a\#}}$) and 0.34 ($\Delta G_{\text{a\#}}$) kcal mol⁻¹ when considering BSSE correction. The result shows that the M06-2X method in combination with the BSSE correction afford energies similar to those determined by the accurate and well recognized CCSD(T) level calculation. Considering the computational costs, the M06-2X/def2-TZVP method is selected to perform the single-point energy calculation for the title reaction system. As shown in Table 1, the barrier differences between the computational and literature ones that were derived from the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(2df,2p) method (Anglada et al., 2016) are 0.5-1.0 kcal mol⁻¹. Such discrepancies may be attributed to the different theoretical method used in computing energies. The barrier of Entry 4 is 3.3 kcal mol⁻¹, which is lower than the corresponding CCSD(T)/CBS result by 0.5 kcal mol⁻¹ (Anglada et al., 2016). The results show that the M06-2X method provides energies similar to those determined by the CCSD(T) level calculation. Table 1 Relative free-energies (kcal mol⁻¹) for the stationary points and free-energy ($\Delta G_{\text{a\#}}$) barriers for the elementary pathways of distinct carbonyl oxides reactions with water dimer calculated at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory. Labels A, B, C, and D are defined in Figure 1

Entry	R1	R2	DO2H4O4H3	DO4H2O3H1	A	B	C	D	$\Delta G_{\text{a\#}}$
1	H	H	-123.6	96.7	-2.5	(-2.9)	0.2	-40.5	-39.9
2	[2.2]	2	H	H	124.5	-94.9	-2.5	(-3.0)	0.2
3	H	H	-143.8	-116.9	-2.2	(-2.6)	0.2	-39.1	-40.2
4	H	H	143.0	122.7	-1.9	(-2.3)	1.4	-40.0	-40.3

3.3 {3.8} 5 CH₃ H -126.2 100.9 -2.5(-3.0) 4.1 -32.4 -31.9 6.6 [6.0] 6 CH₃ H 130.0 -90.4 -2.0(-2.5) 4.3 -31.6 -32.2 6.3 7 CH₃ H -146.0 -116.3 -2.1(-2.6) 4.1 -30.9 -32.2 6.2 8 CH₃ H 138.1 126.3 -2.3(-2.8) 4.7 -31.7 -31.9 7.0 9 H CH₃ -122.1 95.0 -4.3(-4.8) 0.6 -36.6 -36.2 4.9 [3.9] 10 H CH₃ 125.6 -93.6 -3.9(-4.3) 0.7 -35.7 -36.5 4.6 11 H CH₃ -138.1 -120.5 -4.4(-4.9) 1.1 -34.9 -36.5 5.5 12 H CH₃ 139.2 123.4 -3.6(-4.1) 2.0 -36.0 -36.2 5.6 13 CH₃ CH₃ -125.4 101.5 -4.6(-5.1) 4.2 -29.7 -29.1 8.8 [7.8] 14 CH₃ CH₃ 128.5 -89.8 -4.2(-4.8) 4.5 -28.6 -29.7 8.7 15 CH₃ CH₃ -145.4 -117.6 -4.9(-5.3) 4.6 -28.2 -29.7 9.5 16 CH₃ CH₃ 136.3 129.4 -4.5(-5.0) 5.2 -29.2 -29.1 9.7 Values in parenthesis correspond to without considering the BSSE correction, values in brackets correspond to CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(2df,2p), values in braces correspond to CCSD(T)/CBS//B3LYP/6-311+G(2df,2p) Table S1 Y/X (Y = M06-2X, CCSD(T), X = 6-311+G(2df,2p), def2-TZVP) calculated energy barrier ($\Delta E_{a\#}$, $\Delta G_{a\#}$) for the addition reactions of carbonyl oxides with HHPs based on the M06-2X/6-311+G(2df,2p) optimized geometries (kcal \cdot mol⁻¹) Reactions CCSD(T)/6-311+G(2df,2p) M06-2X/def2-TZVP $\Delta E_{a\#}$ $\Delta G_{a\#}$ $\Delta E_{a\#}$ $\Delta G_{a\#}$ R1a 9.4a; 7.9b 10.1a; 8.6b 8.0a; 7.6b 8.8a; 8.4b R1b 13.0a; 11.6b 13.3a; 11.9b 11.9a; 11.4b 12.2a; 11.7b R1c 8.1a; 6.7b 9.2a; 7.8b 6.9a; 6.4b 7.9a; 7.4b R1d 8.6a; 7.6b 10.2a; 9.2b 7.0a; 6.7b 8.7a; 8.4b R3a 6.6a; 4.9b 7.1a; 5.4b 5.8a; 4.4b 6.2a; 5.8b R3b 8.4a; 7.3b 9.7a; 8.6b 7.3a; 6.8b 8.8a; 8.3b R3c 6.5a; 4.8b 7.3a; 5.6b 5.8a; 5.4b 6.6a; 6.2b R3d 8.4a; 6.8b 9.7a; 8.1b 7.3a; 6.8b 8.6a; 8.1b R5a 12.3a; 10.9b 13.2a; 11.8b 11.5a; 11.1b 12.5a; 12.1b R5b 11.0a; 9.4b 12.4a; 10.8b 10.6a; 10.1b 12.0a; 11.5b R5c 12.0a; 10.6b 13.3a; 11.9b 11.3a; 10.9b 12.5a; 12.1b R5d 12.2a; 11.0b 13.8a; 12.6b 11.4a; 11.0b 13.0a; 12.6b a and b represent without and with considering the BSSE correction 5. Regarding the kinetics, the authors should clarify if they have considered the pre-reactive complexes in the kinetic study and if they play a role in the temperature dependence of the rate constants. Response: As shown in Figure 5, the CH₂OO + HO-CH₂OO-H (Pa1) reaction proceeds according to a two-step mechanism: (i) a fast thermal equilibrium between the reactants and intermediate IM1a, (ii) the addition of CH₂OO leading to the formation of product P1a. The whole reaction process is expressed as follows: (5) Applying the steady state approximation

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(SSA) for the intermediate IM1a, the overall rate coefficient is extrapolated to the eqn (6): (Zhang et al., 2012; Liu et al., 2015) (6) If $k_2 \ll k_{-1}$, the overall rate coefficient is written as follows: (Ryzhkov et al., 2006; Chen et al., 2016) (7) The equilibrium coefficient K_{eq} is expressed as eqn (8): (8) where σ is reaction symmetry number, $Q_{IM}(T)$, $Q_A(T)$ and $Q_B(T)$ denote the products of electronic, translational, rotational, torsional, and vibrational canonical partition functions for the intermediate, reactants A and B, respectively (Mendes, et al., 2014), T is the temperature in Kelvin, G_R and G_{IM} are the total free-energies of the reactant and intermediate, respectively. Table R1 lists the partition functions, equilibrium coefficients (K_{eq}), and rate coefficients ($k_2(\text{IM1a-TS1a})$ and $k_{ovr}(\text{R1a})$) of the bimolecular reaction of CH_2OO with $\text{HO-CH}_2\text{OO-H}$ (Pa1). As shown the Table R1, the partition functions of reactants and intermediate increase with raising temperature, whereas the $k_{ovr}(\text{R1a})$, K_{eq} and $k_2(\text{IM1a-TS1a})$ decrease with increasing temperature, indicating that there is not a direct correlation between $k_{ovr}(\text{R1a})$ and partition function of pre-reactive intermediate. The result shows that the kinetics parameters strongly depend on the interaction between K_{eq} and $k_2(\text{IM1a-TS1a})$. Similar conclusions are also obtained from those of the anti- $\text{CH}_3\text{CHOO} + \text{HO-CH}_2\text{OO-H}$ (R9), syn- $\text{CH}_3\text{CHOO} + \text{HO-CH}_2\text{OO-H}$ (R10) and $(\text{CH}_3)_2\text{CHOO} + \text{HO-CH}_2\text{OO-H}$ (R11) systems (Table R2-R4). Table R1 The partition function, equilibrium coefficient (K_{eq}) ($\text{cm}^3 \text{ molecule}^{-1}$), and rate coefficients ($k_2(\text{IM1a-TS1a})$ and $k_{ovr}(\text{R1a})$) ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of CH_2OO reactions with $\text{HO-CH}_2\text{OO-H}$ (Pa1) computed at different temperatures T/K

T/K	$Q_{\text{CH}_2\text{OO}}$	$Q_{\text{HOCH}_2\text{OOH}}$	Q_{IMa}	K_{eq}	$k_2(\text{IM1a-TS1a})$	$k_{ovr}(\text{R1a})$
273	7.9×10^{10}	1.6	1.1×10^{15}	2.8×10^{-6}	4.3×10^{-6}	1.2×10^{-11}
280	8.8×10^{10}	1.9	1.1×10^{15}	1.5×10^{-6}	2.4×10^{-6}	4.0×10^{-6}
298	1.2×10^{11}	2.7	1.1×10^{15}	1.6×10^{-6}	3.3×10^{-6}	5.4×10^{-6}
300	1.2×10^{11}	2.8	1.1×10^{15}	1.6×10^{-6}	3.2×10^{-6}	5.1×10^{-6}
320	1.6×10^{11}	4.2	1.1×10^{15}	1.1×10^{-6}	2.7×10^{-6}	3.0×10^{-6}
340	2.1×10^{11}	6.2	1.1×10^{16}	8.1×10^{-7}	2.3×10^{-6}	1.9×10^{-6}
360	2.7×10^{11}	9.0	1.1×10^{16}	6.2×10^{-7}	2.0×10^{-6}	1.2×10^{-6}
380	3.5×10^{11}	1.3	1.1×10^{16}	3.6×10^{-7}	1.8×10^{-6}	8.6×10^{-7}
400	4.5×10^{11}	1.8	1.1×10^{16}	1.8×10^{-7}	1.6×10^{-6}	6.3×10^{-7}

Table R2 The partition function, equilibrium coefficient (K_{eq}) (cm³ molecule⁻¹), and rate coefficients (k₂(IM9-TS9) and k_{ovr}(R9)) (cm³ molecule⁻¹ s⁻¹) of anti-CH₃CHO reactions with HO-CH₂OO-H (Pa1) computed at different temperatures T/K

T/K	Qanti-CH ₃ CHO	QH ₂ O	QHOCH ₂ OOH	QIM9	K _{eq}	k ₂ (IM9-TS9)	k _{ovr} (R9)
273	1.4 × 10 ¹²	1.6 × 10 ¹²	9.1 × 10 ¹⁵	1.3 × 10 ⁻⁴	4.4 × 10 ⁻⁵	5.5 × 10 ⁻⁹	280 1.6 × 10 ¹²
280	1.9 × 10 ¹²	1.2 × 10 ¹⁶	9.6 × 10 ⁻⁵	3.9 × 10 ⁻⁵	3.7 × 10 ⁻⁹	298 2.4 × 10 ¹²	2.7 × 10 ¹²
298	2.5 × 10 ¹⁶	5.0 × 10 ⁻⁵	2.9 × 10 ⁻⁵	1.5 × 10 ⁻⁹	300 2.5 × 10 ¹²	2.8 × 10 ¹²	2.7 × 10 ¹⁶
300	4.7 × 10 ⁻⁵	2.9 × 10 ⁻⁵	1.3 × 10 ⁻⁹	320 3.7 × 10 ¹²	4.2 × 10 ¹²	5.8 × 10 ¹⁶	2.5 × 10 ⁻⁵
320	2.2 × 10 ⁻⁵	5.5 × 10 ⁻⁵	10 ⁻¹⁰	340 5.4 × 10 ¹²	6.2 × 10 ¹²	1.2 × 10 ¹⁷	1.5 × 10 ⁻⁵
360	1.7 × 10 ⁻⁵	2.6 × 10 ⁻¹⁰	360 7.8 × 10 ¹²	9.0 × 10 ¹²	2.5 × 10 ¹⁷	9.1 × 10 ⁻⁶	1.4 × 10 ⁻⁵
380	1.1 × 10 ¹³	1.3 × 10 ⁻¹⁰	380 1.3 × 10 ¹³	5.1 × 10 ¹⁷	5.9 × 10 ⁻⁶	1.2 × 10 ⁻⁵	7.1 × 10 ⁻¹¹
400	1.6 × 10 ¹³	1.8 × 10 ¹³	1.0 × 10 ¹⁸	4.1 × 10 ⁻⁶	1.0 × 10 ⁻⁵	4.1 × 10 ⁻¹¹	

Table R3 The partition function, equilibrium coefficient (K_{eq}) (cm³ molecule⁻¹), and rate coefficients (k₂(IM10-TS10) and k_{ovr}(R10)) (cm³ molecule⁻¹ s⁻¹) of syn-CH₃CHO reactions with HO-CH₂OO-H (Pa1) computed at different temperatures T/K

T/K	Qsyn-CH ₃ CHO	QH ₂ O	QIM10	K _{eq}	k ₂ (IM10-TS10)	k _{ovr} (R10)
273	1.0 × 10 ¹²	1.6 × 10 ¹²	6.6 × 10 ¹⁵	1.5 × 10 ⁻⁶	5.6 × 10 ⁻⁹	8.1 × 10 ⁻¹⁵
280	1.2 × 10 ¹²	1.9 × 10 ¹⁵	8.8 × 10 ¹⁵	1.2 × 10 ⁻⁶	6.0 × 10 ⁻⁹	7.5 × 10 ⁻¹⁵
298	1.7 × 10 ¹²	2.7 × 10 ¹⁵	1.8 × 10 ¹⁶	1.7 × 10 ⁻⁶	6.3 × 10 ⁻⁹	300 1.8 × 10 ¹²
300	2.8 × 10 ¹²	1.9 × 10 ¹⁶	8.3 × 10 ⁻⁷	7.5 × 10 ⁻⁹	6.2 × 10 ⁻¹⁵	320 2.6 × 10 ¹²
320	4.2 × 10 ¹²	4.1 × 10 ¹⁶	8.3 × 10 ⁻⁷	7.5 × 10 ⁻⁹	6.2 × 10 ⁻¹⁵	340 3.7 × 10 ¹²
360	6.2 × 10 ¹²	8.7 × 10 ¹⁶	4.3 × 10 ⁻⁷	1.1 × 10 ⁻⁸	4.6 × 10 ⁻¹⁵	360 5.3 × 10 ¹²
380	9.0 × 10 ¹²	1.8 × 10 ¹⁷	3.3 × 10 ⁻⁷	1.3 × 10 ⁻⁸	4.1 × 10 ⁻¹⁵	380 7.5 × 10 ¹²
400	1.3 × 10 ¹³	3.6 × 10 ¹⁷	2.6 × 10 ⁻⁷	1.5 × 10 ⁻⁸	3.8 × 10 ⁻¹⁵	400 1.1 × 10 ¹³
	1.8 × 10 ¹³	7.2 × 10 ¹⁷	2.1 × 10 ⁻⁷	1.7 × 10 ⁻⁸	3.5 × 10 ⁻¹⁵	

Table R4 The partition function, equilibrium coefficient (K_{eq}) (cm³ molecule⁻¹), and rate coefficients (k₂(IM11-TS11) and k_{ovr}(R11)) (cm³ molecule⁻¹ s⁻¹) of (CH₃)₂CHO reactions with HO-CH₂OO-H (Pa1) computed at different temperatures T/K

T/K	Q(CH ₃) ₂ CHO	QH ₂ O	QIM11	K _{eq}	k ₂ (IM11-TS11)	k _{ovr} (R11)
273	7.2 × 10 ¹²					

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1012 1.6×10^{12} 4.0 $\times 10^{16}$ 8.8 $\times 10^{-5}$ 3.1 $\times 10^{-8}$ 2.7 $\times 10^{-12}$ 280 8.5 $\times 10^{12}$ 1.9 \times
1012 5.5 $\times 10^{16}$ 6.9 $\times 10^{-5}$ 3.4 $\times 10^{-8}$ 2.3 $\times 10^{-12}$ 298 1.3 $\times 10^{13}$ 2.7 $\times 10^{12}$ 1.2 \times
1017 3.7 $\times 10^{-5}$ 4.1 $\times 10^{-8}$ 1.5 $\times 10^{-12}$ 300 1.4 $\times 10^{13}$ 2.8 $\times 10^{12}$ 1.3 $\times 10^{17}$ 3.5 \times
10⁻⁵ 4.2 $\times 10^{-8}$ 1.5 $\times 10^{-12}$ 320 2.2 $\times 10^{13}$ 4.2 $\times 10^{12}$ 3.2 $\times 10^{17}$ 1.9 $\times 10^{-5}$ 5.2 \times
10⁻⁸ 1.0 $\times 10^{-12}$ 340 3.5 $\times 10^{13}$ 6.2 $\times 10^{12}$ 7.3 $\times 10^{17}$ 1.2 $\times 10^{-5}$ 6.2 $\times 10^{-8}$ 7.2 \times
10⁻¹³ 360 5.5 $\times 10^{13}$ 9.0 $\times 10^{12}$ 1.7 $\times 10^{18}$ 7.4 $\times 10^{-6}$ 7.4 $\times 10^{-8}$ 5.4 $\times 10^{-13}$ 380
8.6 $\times 10^{13}$ 1.3 $\times 10^{13}$ 3.8 $\times 10^{18}$ 5.0 $\times 10^{-6}$ 8.6 $\times 10^{-8}$ 4.2 $\times 10^{-13}$ 400 1.3 $\times 10^{14}$
1.8 $\times 10^{13}$ 8.3 $\times 10^{18}$ 3.5 $\times 10^{-6}$ 9.8 $\times 10^{-8}$ 3.4 $\times 10^{-13}$ The corresponding sen-
tences have been added in the page 9 line 219-237 of the revised manuscript in blue
color: As shown in Figure 5, the CH₂OO + HO-CH₂OO-H (Pa1) reaction proceeds ac-
cording to a two-step mechanism: (i) a fast thermal equilibrium between the reactants
and intermediate IM1a, (ii) the addition of CH₂OO leading to the formation of product
P1a. The whole reaction process is expressed as follows: (4) Applying the steady state
approximation (SSA) for the intermediate IM1a, the overall rate coefficient is extrap-
olated to the eqn (5) (Zhang et al., 2012; Liu et al., 2015) (5) If $k_2 \ll k_{-1}$, the overall
rate coefficient is written as follows: (Chen et al., 2016b; Ryzhkov et al., 2006) (6) The
equilibrium coefficient K_{eq} is expressed as eqn (7): (7) where σ is reaction symmetry
number, $Q_{IM}(T)$, $Q_A(T)$ and $Q_B(T)$ denote the products of electronic, translational, ro-
tational, torsional, and vibrational canonical partition functions for the intermediate, re-
actants A and B, respectively (Mendes et al., 2014), T is the temperature in Kelvin, GR
and G_{IM} are the total free-energies of the reactant and complex, respectively. 6. The
authors report rate constants for the reactions of the carbonyl oxides considered with
HHP's (Table 2), but no mention is done for the reactions of P1x with Carbonyl oxides.
Moreover, that authors should clarify if they have considered all different conformers of
the stationary points in the kinetic study. In addition, they should estimate the errors
in the these calculated rate constants, since they can be between one and two orders
of magnitude according to the errors in the computed free energy barriers. Response:
Based on the Reviewer's suggestion, the rate coefficients of carbonyl oxides reactions
with P1x, P3x, P5x, and P7x are calculated using a combination of canonical transition

state theory (CTST) and an asymmetric Eckart tunneling correction at 273-400 K. And the different conformers of stationary points in the kinetics study are taken into account, with the obtained results listed in Table S5-S8. As shown in Table S5, the predicted rate coefficients for the reaction of CH₂OO with P1a decrease with increasing temperature, with a similar trend observed for CH₂OO + P1b, CH₂OO + P1c and CH₂OO + P1d systems. The result implies that the oligomer formation from CH₂OO reaction with HHP is preferable under low temperature conditions. Similar conclusions are obtained from the anti-CH₃CHOO + P3x (Table S6), syn-CH₃CHOO + P5x (Table S7) and (CH₃)₂CHOO + P7x (Table S8) systems. In order to avoid redundancy, we do not repeat them here in detail. Considering the errors of the computed free energy barriers, the uncertainty of rate coefficient is estimated within an order of magnitude. Corresponding descriptions have been added in the page 18 line 500-506 and page 19 line 521-528 of the revised manuscript: the rate coefficients of distinct SCI reactions with HO-CH₂OO-H (Pa1) are computed using a combination of canonical transition state theory (CTST) and an asymmetric Eckart tunneling correction based on the free energies obtained at the M06-2X level, in the temperature range from 273 to 400 K. And the different conformers of stationary points in the kinetics study are taken into account, with the results listed in Table 2 and Table S5-S8. As shown in Table S5, the rate coefficients of CH₂OO + P1a, CH₂OO + P1b, CH₂OO + P1c and CH₂OO + P1d reactions decrease with increasing temperature, indicating that the oligomer formation from CH₂OO reactions with HHP is preferable under low temperature conditions. Similar conclusions are also obtained from the anti-CH₃CHOO + P3x (Table S6), syn-CH₃CHOO + P5x (Table S7) and (CH₃)₂CHOO + P7x (Table S8) systems. In order to avoid redundancy, we do not repeat them here in detail. Considering the errors of the computed free energy barriers, the uncertainty of rate coefficient is estimated within an order of magnitude. Table S5 Rate coefficients (cm³ molecule⁻¹ s⁻¹) of CH₂OO reactions with P1a, P1b, P1c and P1d computed at different temperatures T/K

T/K	k(CH ₂ OO+P1a)	k(CH ₂ OO+P1b)	k(CH ₂ OO+P1c)	k(CH ₂ OO+P1d)
273	5.1 × 10 ⁻¹²	3.5 × 10 ⁻¹²	8.2 × 10 ⁻¹³	4.8 × 10 ⁻¹¹
280	4.0 × 10 ⁻¹²	2.9 × 10 ⁻¹²	7.1 × 10 ⁻¹³	3.7 × 10 ⁻¹¹
298	2.3 × 10 ⁻¹²	1.9 × 10 ⁻¹²		

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5.2×10^{-13} 1.9×10^{-11} 300 2.2×10^{-12} 1.8×10^{-12} 5.0×10^{-13} 1.8×10^{-11} 320
 1.3×10^{-12} 1.2×10^{-12} 3.7×10^{-13} 1.0×10^{-11} 340 8.3×10^{-13} 8.5×10^{-13} $2.8 \times$
 10^{-13} 5.9×10^{-12} 360 5.6×10^{-13} 6.3×10^{-13} 2.3×10^{-13} 3.8×10^{-12} 380 $4.0 \times$
 10^{-13} 4.9×10^{-13} 1.9×10^{-13} 2.5×10^{-12} 400 3.0×10^{-13} 3.9×10^{-13} 1.6×10^{-13}
 1.8×10^{-12}

Table S6 Rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of anti- CH_3CHOO reactions with P3a,
 P3b, P3c and P3d computed at different temperatures T/K k(anti+P3a) k(anti+P3b)
 k(anti+P3c) k(anti+P3d) 273 3.5×10^{-9} 2.3×10^{-9} 1.7×10^{-7} 2.1×10^{-9} 280 $2.3 \times$
 10^{-9} 1.4×10^{-9} 1.0×10^{-7} 1.4×10^{-9} 298 8.8×10^{-10} 5.8×10^{-10} 2.9×10^{-8} 5.9
 $\times 10^{-10}$ 300 8.0×10^{-10} 5.3×10^{-10} 2.6×10^{-8} 5.4×10^{-10} 320 3.2×10^{-10} $2.3 \times$
 10^{-10} 7.9×10^{-9} 2.3×10^{-10} 340 1.4×10^{-10} 1.1×10^{-10} 2.8×10^{-9} 1.1×10^{-10}
 360 7.1×10^{-11} 5.8×10^{-11} 1.1×10^{-9} 5.9×10^{-11} 380 3.8×10^{-11} 3.3×10^{-11} 4.9
 $\times 10^{-10}$ 3.4×10^{-11} 400 2.2×10^{-11} 2.0×10^{-11} 2.4×10^{-10} 2.0×10^{-11}

Table S7 Rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of syn- CH_3CHOO reactions with P5a,
 P5b, P5c and P5d computed at different temperatures T/K k(syn+P5a) k(syn+P5b)
 k(syn+P5c) k(syn+P5d) 273 2.1×10^{-11} 1.7×10^{-13} 2.1×10^{-11} 2.4×10^{-13} 280
 1.5×10^{-11} 1.4×10^{-13} 1.5×10^{-11} 2.0×10^{-13} 298 7.5×10^{-12} 1.0×10^{-13} $7.6 \times$
 10^{-12} 1.4×10^{-13} 300 6.9×10^{-12} 9.7×10^{-14} 7.0×10^{-12} 1.4×10^{-13} 320 $3.5 \times$
 10^{-12} 6.9×10^{-14} 3.6×10^{-12} 9.6×10^{-14} 340 1.9×10^{-12} 5.2×10^{-14} 2.0×10^{-12}
 7.1×10^{-14} 360 1.1×10^{-12} 4.0×10^{-14} 1.2×10^{-12} 5.5×10^{-14} 380 7.1×10^{-13}
 3.0×10^{-14} 7.3×10^{-13} 4.4×10^{-14} 400 4.7×10^{-13} 2.6×10^{-14} 4.9×10^{-13} $3.6 \times$
 10^{-14}

Table S8 Rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of $(\text{CH}_3)_2\text{CHOO}$ reactions with P7a,
 P7b, P7c and P7d computed at different temperatures T/K k($(\text{CH}_3)_2\text{CHOO} + \text{P7a}$)
 k($(\text{CH}_3)_2\text{CHOO} + \text{P7b}$) k($(\text{CH}_3)_2\text{CHOO} + \text{P7c}$) k($(\text{CH}_3)_2\text{CHOO} + \text{P7d}$) 273 $7.8 \times 10^{-$
 14 9.1×10^{-14} 1.8×10^{-12} 4.5×10^{-13} 280 6.8×10^{-14} 8.2×10^{-14} 1.5×10^{-12}
 3.9×10^{-13} 298 5.0×10^{-14} 6.6×10^{-14} 1.0×10^{-12} 2.8×10^{-13} 300 $4.8 \times 10^{-$
 14 6.5×10^{-14} 9.9×10^{-13} 2.7×10^{-13} 320 3.6×10^{-14} 5.3×10^{-14} 6.9×10^{-13}

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1.9×10^{-13} 340 2.8×10^{-14} 4.5×10^{-14} 5.1×10^{-13} 1.5×10^{-13} 360 2.2×10^{-14}
 3.9×10^{-14} 3.9×10^{-13} 1.2×10^{-13} 380 1.9×10^{-14} 3.5×10^{-14} 3.1×10^{-13} 9.6
 $\times 10^{-14}$ 400 1.6×10^{-14} 3.1×10^{-14} 2.5×10^{-13} 8.0×10^{-14} 7. With respect to the atmospheric implications, the authors compare the reaction rates of the reaction investigated with those between carbonyl oxides with formic acid. In my opinion, the reactions rates of carbonyl oxides with water and water dimer, but also the reactions rates of HHPs with water should be also taken into account, because the high concentration of water vapor in the atmosphere. For the last, there are free energy barriers in the literature to compare with. Response: As shown in Table 2, the rate coefficient of anti-CH₃CHO + Pa1 reaction (R9) is significantly higher than that of the other three pathways (R1a, R10 and R11). Therefore, it would be interesting to investigate whether the anti-CH₃CHO + Pa1 reaction can compete well with the anti-CH₃CHO + (H₂O)₂ (R12) system because the latter reaction is the dominant chemical sink (Anglada et al., 2016; Taatjes, et al., 2013). The ratio of reaction rates of R9 and R12 is expressed as follows (9) The room temperature rate coefficient k_{R9} is 1.5×10^{-9} cm³ molecule⁻¹ s⁻¹. Assuming that the concentration of Pa1 is approximately equal to that of SCIs ($\sim 5.0 \times 10^4$ molecules cm⁻³, within an order of magnitude uncertainty) in the boreal forest and rural environments of Finland and Germany (Novelli et al, 2016, 2017). The atmospheric lifetime of anti-CH₃CHO reactivity toward Pa1 can be estimated as 1.3×10^3 s. The experimental rate coefficient of reaction R12 approximately equals $\sim 1.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K (Lin et al., 2016). The concentration of water dimer is 5.5×10^{13} molecules cm⁻³ at 3 km altitude (Long et al., 2016). The ν_{R9}/ν_{R12} ratio is less than 1.4%, meaning that the anti-CH₃CHO + Pa1 reaction is minor loss process in the atmosphere. However, the [(H₂O)₂] is very low at the altitude above 15 km ($< 2.7 \times 10^6$ molecules cm⁻³) (Long et al., 2016), the anti-CH₃CHO + Pa1 reaction can compete well with the anti-CH₃CHO + (H₂O)₂ reaction, and thus contribute to the formation and growth of SOA. Kumar et al. (2014) proposed that the gas-phase decomposition of Pa1 has two competitive pathways, namely (i) HO-CH₂OO-H \rightarrow CH₂O + H₂O₂ and (ii) HO-CH₂OO-H \rightarrow HCOOH + H₂O.

The free energy barriers $\Delta G_{\#}$ in the presence of a single water molecule are 31.2 and 47.8 kcal mol⁻¹, respectively, which are 13.5 and 10.2 kcal mol⁻¹ lower than the uncatalyzed reactions. The result reveals that the formaldehyde-forming channel is preferable in the absence and presence of water molecule, and the role of water catalysis on the gas-phase Pa1 decomposition is significant. The $\Delta G_{\#}$ of bimolecular reaction of anti-CH₃CHOO with Pa1 is 7.3 kcal mol⁻¹, which is 23.9 kcal mol⁻¹ lower than the formaldehyde-forming channel. It is concluded that the Pa1 + H₂O reaction is less competitive as compared to the anti-CH₃CHOO + Pa1 system. Corresponding descriptions have been added in the page 20 line 542-556, page 20 line 565 and page 21 line 566-579 of the revised manuscript: As discussed above, the anti-CH₃CHOO + HO-CH₂OO-H (Pa1) reaction (R9) is preferred over the other three pathways (R1a, R10 and R11). Therefore, it would be interesting to investigate whether the anti-CH₃CHOO + Pa1 reaction can compete well with the anti-CH₃CHOO + (H₂O)₂ (R12) system because the latter reaction is the dominant chemical sink (Taatjes et al., 2013; Anglada et al., 2016). The ratio of reaction rates of R9 and R12 is expressed as follows (10) The room temperature rate coefficient k_{R9} is 1.5×10^{-9} cm³ molecule⁻¹ s⁻¹. Assuming that the concentration of Pa1 is approximately equal to that of SCIs ($\sim 5.0 \times 10^4$ molecules cm⁻³, within an order of magnitude uncertainty) in the boreal forest and rural environments of Finland and Germany (Novelli et al., 2016; 2017). The atmospheric lifetime of anti-CH₃CHOO reactivity toward Pa1 can be estimated as 1.3×10^3 s. The experimental rate coefficient of reaction R12 approximately equals $\sim 1.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K (Lin et al., 2016). The concentration of water dimer is 5.5×10^{13} molecules cm⁻³ at 3 km altitude (Long et al., 2016). The ν_{R9}/ν_{R12} ratio is less than 1.4% when the [(H₂O)₂] is $\sim 10^{13}$ molecules cm⁻³, meaning that the anti-CH₃CHOO + Pa1 reaction is minor loss process in the atmosphere. However, the [(H₂O)₂] is very low at the altitude above 15 km, the anti-CH₃CHOO + Pa1 reaction can compete well with the anti-CH₃CHOO + (H₂O)₂ reaction, and thus contribute to the formation and growth of SOA. Kumar et al. (2014) proposed that the gas-phase decomposition of Pa1 has two competitive pathways: (i) HO-CH₂OO-H →

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CH₂O + H₂O₂ and (ii) HO-CH₂OO-H → HCOOH + H₂O. The ΔG_{a‡} in the presence of a single water molecule are 31.2 and 47.8 kcal mol⁻¹, respectively, which are 13.5 and 10.2 kcal mol⁻¹ lower than the uncatalyzed reactions. The result reveals that the formaldehyde-forming channel is preferable in the absence and presence of water molecule, and the role of water catalysis on the gas-phase decomposition of Pa1 is significant. The ΔG_{a‡} of bimolecular reaction of anti-CH₃CHOO with Pa1 is 7.3 kcal mol⁻¹, which is 23.9 kcal mol⁻¹ lower than the formaldehyde-forming channel. It is concluded that the Pa1 + H₂O reaction is less competitive as compared to the anti-CH₃CHOO + Pa1 system. 8. An hydrogen misses in the structure of P1a in Figure 2. In addition some addition structures of the P2x compounds should be drawn if the different figures and the numbers should have a larger size. Response: Based on the Reviewer's suggestion, the PES of CH₂OO reaction with HO-CH₂OO-H (Pa1) is redrawn in Figure 2, and the str in the Figure 2.

Figure 2. PES (ΔG and ΔE (italic)) for the reaction of CH₂OO with HO-CH₂OO-H (Pa1) computed at the M06-2X/def2-TZVP//M06-2X/6-311+G(2df,2p) level of theory

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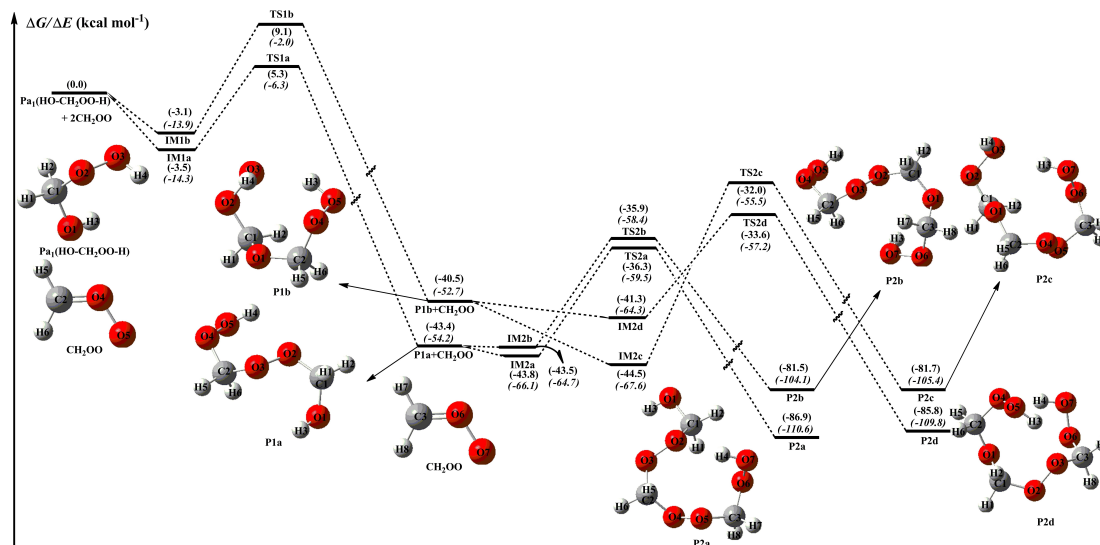


Fig. 1.

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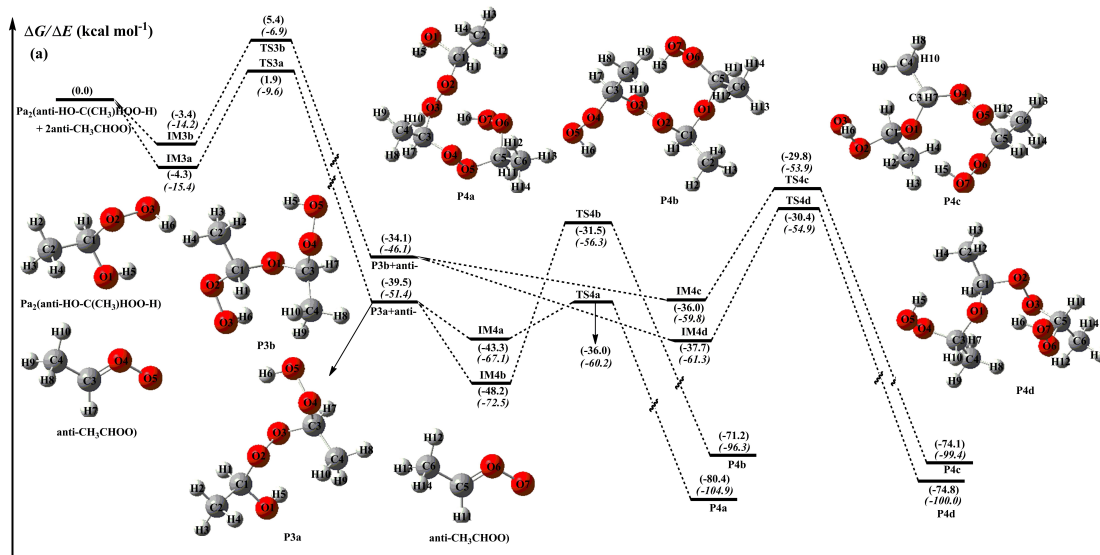


Fig. 2.

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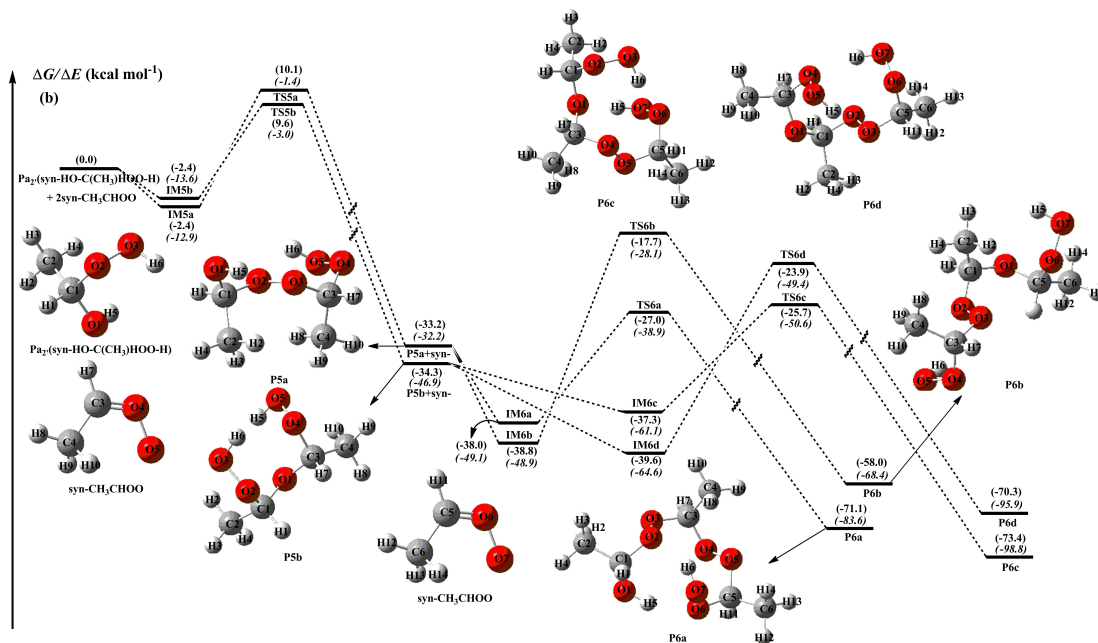


Fig. 3.

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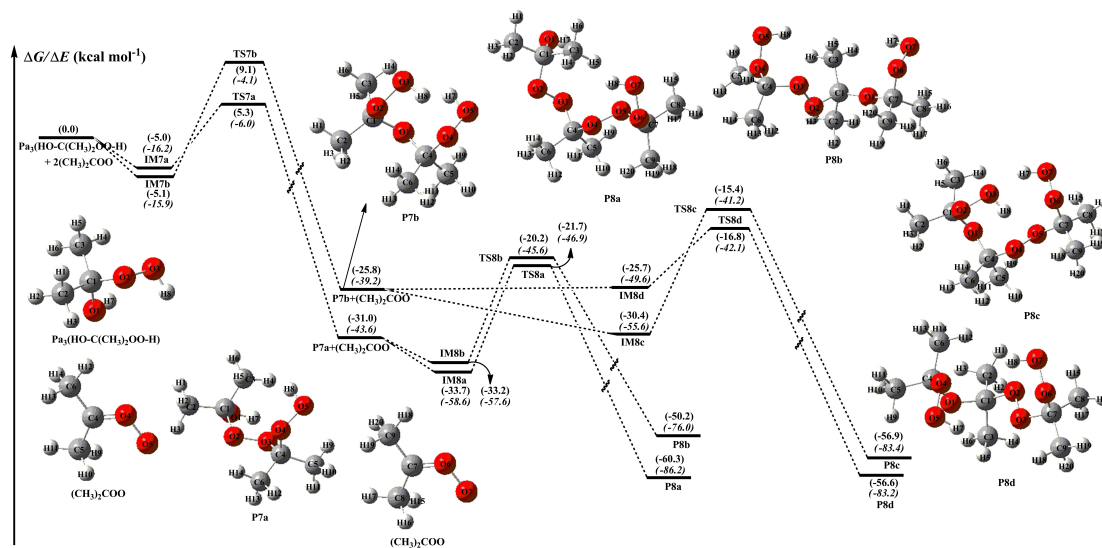


Fig. 4.

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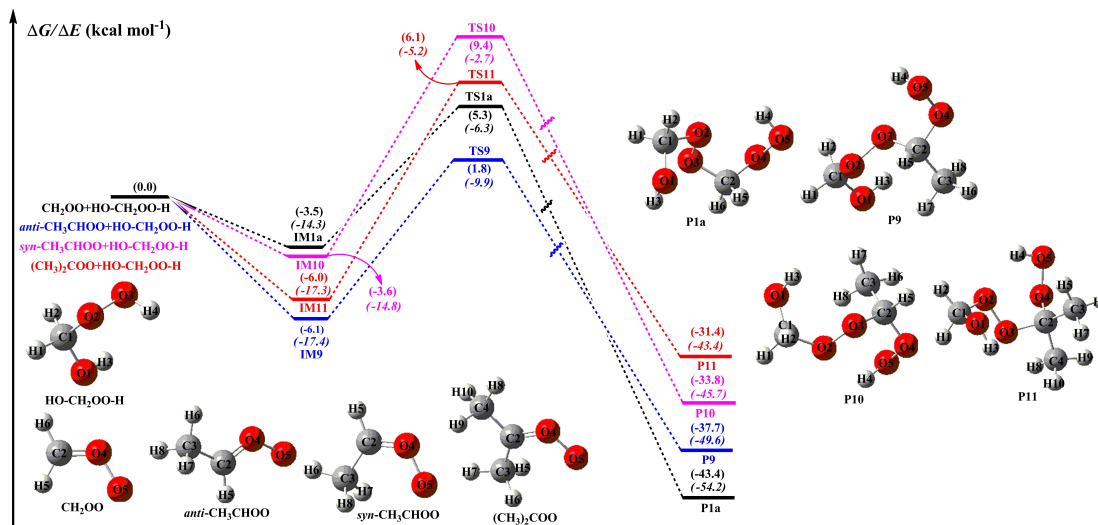


Fig. 5.

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