Supplement of Atmos. Chem. Phys., 26, 6973–6992, 2026
https://doi.org/10.5194/acp-26-6973-2026-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Reactions of carbonyl oxide with aldehydes: accurate electronic structure methods, kinetic insights, and atmospheric implications

Chaolu Xie and Bo Long

Correspondence to: Bo Long (wwwltcommon@sina.com)

CONTENTS

The method GMMQ.L4 is extension of previous investigations. The GMM(P).L1 (Long et al., 2022), GMM(P).L2 (Long et al., 2023) and GMMQ.L3 (Xia et al., 2025) was completed by Long et al., and Xia et al.

Details of reaction R9

The enthalpy of activation for tight transition state of R9 were calculated to be −9.74 kcal/mol at M11-L/MG3S level as the DF-CCSD(T)-F12b/jun-cc-pVDZ optimization converges to the product. We did not focus on finding a tight transition state because we found that this transition state had almost no effect on the overall rate constant due to the low energy barrier.

Table A1. Explanations for details in kinetics.

Kinetics methods	Explanation	Ref.
anharmonicity	A factor to scale vibrational frequencies for calculating the zero-point energy and vibrational partition functions	(Long et al., 2023)
re-crossing	Probability of transition state to pre-reaction complex	(Zheng and Truhlar, 2012)
dual-level strategy	The combination of conventional transition state theory (TST) at HL with canonical variational transition state theory with small-curvature tunneling (CVT/SCT) at LL	(Long et al., 2016, 2019; Sun et al., 2024)
multi-structural anharmonicity	The effect of multiple conformations on rate constants	(Zheng et al., 2012)

Table S1. The barrier height of TS1 for the components in GMMQ.L4 method in the CH_2OO + HCHO reaction. (in kcal/mol)

Methods	$\Delta V^{\ddagger}$
MW2-F12.L	−8.35
CCSDT-CCSD(T)/cc-pVDZ	0.274
CCSDT-CCSD(T)/cc-pVTZ	0.259
CCSDT-CCSD(T)/CBS	0.252
CCSDT(Q)-CCSDT/cc-pVDZ	0.335
CCSDT(Q)-CCSDT/VTZ(d)	0.297
CCSDT(Q)-CCSDT/CBS	0.281
CCSDTQ-CCSDT(Q)/VDZ(NP)	−0.096
GMMQ.L4	−7.91

Table S2. The relative enthalpies of activation at 0 K for the HCHO + CH_2OO (TS1) and CH_3CHO + CH_2OO (TS2a and TS2b) reactions. (in kcal/mol)

Methods	$\Delta H_0^{\ddagger}$			MUD
	TS1[a]	TS2a[b]	TS2c[b]	
Best Estimate for W2X	−5.62	−5.24	−5.19	0.00
W2X//DF-CCSD(T)-F12b/VDZ(d)	−5.66	−5.24	−5.23	0.03
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.60	−5.35	−5.19	0.04
W2X//DF-CCSD(T)-F12a/cc-pVDZ	−5.72	−5.29	−5.35	0.10
W2X//DF-CCSD(T)-F12b/VDZ(NP)	−6.19	−5.01	−5.82	0.48

[a]The best estimate results are from W2X//CCSD(T)-F12a/cc-pVTZ-F12 for the reaction of CH_2OO + HCHO

[b]The best estimate results are from W2X//CCSD(T)-F12a/cc-pVDZ-F12 for the reaction of CH_2OO + CH_3CHO

Table S3. Standard scale factors for calculating vibrational frequencies different theoretical methods.

Method	Scale Factor
CCSD(T)-F12a/cc-pVTZ-F12	0.984
CCSD(T)-F12a/cc-pVDZ-F12	0.983
DF-CCSD(T)-F12b/jun-cc-pVDZ-F12	0.981
DF-CCSD(T)-F12b/cc-pVDZ	0.977
DF-CCSD(T)-F12b/VDZ(NP)	0.993
DF-CCSD(T)-F12b/VDZ(d)	0.989
M11L/MG3S	0.985

Table S4. Specific Reaction Scale Factors Calculated by Using the M11-L/MG3S Method for HCHO.

	CH_2OO	HCHO	TS
ZPE (Harm)	19.290	16.297	38.298
ZPE (Anh)	19.303	16.130	37.949
$\lambda^{Anh\ a}$	1.001	0.990	0.991
λ_H	0.998	0.998	0.998
$\lambda^{ZPE} = \lambda^{Anh} * \lambda^{H}$	0.999	0.988	0.989

[a] λ^{Anh} equals the ratio of anharmonic zero-point vibrational energy to harmonic zero-point vibrational energy of the M11-L/MG3S method

[b] λ^{ZPE} equals the product of and the generic parameter, where λ_H is obtained from previous studies that gave λ_H equal to 0.998 for CCSD(T)-F12a/cc-pVTZ-F12.

Table S5. Specific Reaction Scale Factors Calculated by Using the MPW1K/6-311 + G(2df,2p) Method for RCHO (R = CH3/C_2H_5/C_3H_7/C_4H_9/C_5H_{11})

	CH_2OO	CH_3CHO	CH_3CH_2CHO	C_4H_7CHO	C_5H_9CHO	$C_6H_{11}CHO$
ZPE (Harm)	20.309	35.743	54.286	72.614	91.072	91.072
ZPE (Anh)	20.072	35.295	53.612	71.723	89.939	89.939
$\lambda^{Anh\ a}$	0.988	0.987	0.988	0.988	0.988	0.988
λ_H	0.997	0.997	0.997	0.997	0.997	0.997
$\lambda^{ZPE} = \lambda^{Anh} * \lambda$_H	0.985	0.985	0.985	0.985	0.985	0.986
	TS1	TS2c	TS3	TS4	TS5	TS6
ZPE (Harm)	56.837	58.233	76.782	95.016	113.285	113.285
ZPE (Anh)	56.138	57.53	75.817	93.871	111.916	111.916
λ^{Anh}	0.988	0.988	0.987	0.988	0.988	0.988
λ_H	0.997	0.997	0.997	0.997	0.997	0.998
$\lambda^{ZPE} = \lambda^{Anh} * \lambda$_H	0.985	0.985	0.985	0.985	0.985	0.986

[a] λ^{Anh} equals the ratio of anharmonic zero-point vibrational energy to harmonic zero-point vibrational energy of the MPW1K/6-311 + G(2df,2p) method

[b] λ^{ZPE} equals the product of and the generic parameter, where λ_H is obtained from previous studies, which equals to 0.997 for DF-CCSD(T)-F12b/jun-cc-pVDZ and DF-CCSD(T)-F12/jun-cc-pVDZ, and 0.998 for DF-CCSD(T)-F12/VDZ(d).

Table S6. The Lennard-Jone parameters used to calculate the collision rates are as follows.

molecules	σ (in Å)	ε (in K)	Reference
N_2	3.74	82	(Kuwata et al., 2010)
CH_2OO	3.79	520	(Berndt et al., 2015)
HCHO	3.66	385.2	
CH_3CHO	4.94	191.134	

The Lennard-Jones parameter for complex is obtained by the following two formulas:

$$\sigma = \frac{\sigma_1 \sigma_2}{2} \quad (1) \qquad\qquad \varepsilon = \sqrt{\varepsilon_1 \varepsilon_2} \quad (2)$$

σ is the hard-core diameter, and ε is a measure of the strength of the spherically symmetric part of the perturbation.

Table S7. The barrier height of TS1 for the components in MW2-F12.L method in the CH_2OO + HCHO reaction. (in kcal/mol)

Methods	$\Delta V^{\ddagger}$
	MW2-F12.L[a]
HF(CABS)/VQZ-F12	-4.23
CCSD-F12b/VQZ-F12	-7.69
HF(CABS)/V5Z-F12	-4.21
CCSD-F12b/V5Z-F12	-7.64
CCSD/AVQZ	-7.75
CCSD(T)/AVQZ	-8.71
CCSD/AV5Z	-7.64
CCSD(T)/AV5Z	-8.59
CCSD(T)/awCVTZ	-8.79
CCSD(T)(CV)/awCVTZ	-8.67
CCSD(T)/awCVQZ	-8.59
CCSD(T)(CV)/awCVQZ	-8.43
CCSD(T)/aVQZ	-8.71
CCSD(T)CR/aVQZ	-8.69
E[HF][a]	−4.21
E[ΔCCSD][b]	−3.39
E[Δ(T)][c]	−0.95
E[Δ(C+V)][d]	0.19
E[Δ(C+R)][e]	0.01

[a] E[HF] is equals to HF(CABS)/V5Z-F12.

[b] E[ΔCCSD] is equals to (CCSD-F12b/V5Z-F12 - HF(CABS)/V5Z-F12)+((CCSD-F12b/V5Z-F12- HF(CABS)/V5Z-F12)-(CCSD-F12b/VQZ-F12 - HF(CABS)/VQZ-F12))/(1.25^3.2711-1).

[c] E[Δ(T)] is equals to (CCSD(T)/AV5Z - CCSD/AV5Z)+((CCSD(T)/AV5Z - CCSD/AV5Z)-(CCSD(T)/AVQZ - CCSD/AVQZ))/(1.25^3.8270-1).

[d] E[ΔC+V] is equals to (CCSD(T)(CV)/awCVQZ - CCSD(T)/awCVQZ)+((CCSD(T)(CV)/awCVQZ - CCSD(T)/awCVQZ)-(CCSD(T)(CV)/awCVTZ - CCSD(T)/awCVTZ))/(1.3333^3-1).

[e] E[ΔC+R] is equals to CCSD(T)CR/aVQZ - CCSD(T)/aVQZ.

Table S8. The barrier height of TS1 for the components in W2X method in the CH_2OO + HCHO reaction. (in kcal/mol)

Methods	$\Delta V^{\ddagger}$
	W2X
HF(CABS)/7-TZ[a]	-4.25
CCSD-F12b/7-TZ	-7.73
CCSD(T)-F12b/7-TZ	-8.69
HF(CABS)/7-QZ[b]	-4.23
CCSD-F12b/7-QZ	-7.69
MP2/CVTZ(3d)[c]	-9.83
MP2(CR)/CVTZ(3d)	-9.73
MP2/CVDZ(2d)[d]	-11.30
CCSD(T)/CVDZ(2d)	-8.96
MP2(CR)/CVDZ(2d)	-11.38
CCSD(T)(CR)/CVDZ(2d)	-9.03
E[HF][e]	−4.23
E[ΔCCSD][f]	−3.45
E[Δ(T)][g]	−1.00
E[Δ(C+R)][h]	0.13

[a] 7-TZ is VTZ for H, and AVTZ for C and O.

[b] 7-QZ is VQZ for H, and AVQZ for C and O.

[c] CVTZ(3d) is VTZ for H, cc-pCVTZ and cc-pCVQZ for sp and d orbital of C and O.

[d] CVDZ(2d) is VDZ for H, cc-pCVDZ and cc-pCVTZ for sp and d orbital of C and O.

[e] E[HF] is equal to HF(CABS)/7-QZ.

[f] E[ΔCCSD] is equal to (CCSD-F12b/7-QZ - HF(CABS)/7-QZ)-(CCSD-F12b/7-QZ - HF(CABS)/7-QZ)-(CCSD-F12b/7-TZ - HF(CABS)/7-TZ))*4^-5.8769/(4^-5.8769-3^-5.8769)

g E[Δ(T)] is (CCSD(T)-F12b/7-TZ - CCSD-F12b/7-TZ)*1.0607

[h] E[Δ(C+R)] is equal to (MP2(CR)/CVTZ(3d) - MP2/CVTZ(3d))*1.1383+((CCSD(T)(CR)/CVDZ(2d) - CCSD(T)/CVDZ(2d))-(MP2(CR)/CVDZ(2d) - MP2/CVDZ(2d)))*1.5577

Table S9. The enthalpy of activation at 0 K for the transition states of CH_2OO + CH_3CHO reaction by various theoretical methods (in kcal/mol).

Methods	$\Delta H_0^{\ddagger}$		MUD
	TS2a	TS2c	
BE1//CCSD(T)-F12a/cc-pVDZ-F12	−4.90	-4.50	0.00
BE2//CCSD(T)-F12a/cc-pVDZ-F12	−4.60	-4.55	0.15
W3X-L//CCSD(T)-F12a/cc-pVDZ-F12	−5.12	-4.75	0.24
W2X//CCSD(T)-F12a/cc-pVDZ-F12	−5.24	-5.19	0.52
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.35	-5.19	0.57
W2X//DF-CCSD(T)-F12a/cc-pVDZ	−5.29	-5.35	0.62
W2X//DF-CCSD(T)-F12b/VDZ(NP)	−5.01	-5.82	0.72
W2X//DF-CCSD(T)-F12b/VDZ(d)	−5.24	-5.23	0.54
CCSD(T)-F12a/cc-pVDZ-F12	−5.15	-5.04	0.40
DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.82	-4.88	0.66
DF-CCSD(T)-F12a/cc-pVDZ	−6.36	-6.42	1.70
DF-CCSD(T)-F12b/VDZ(NP)	−7.63	-8.38	3.31
DF-CCSD(T)-F12b/VDZ(d)	−6.25	-6.58	1.72
M11-L/MG3S	−4.68	-4.05	0.81
M08-HX/MG3S	−6.61	-6.58	1.90
M06CR/MG3S	−5.61	-3.40	1.16
MN15-L/MG3S	−6.40	-6.43	1.72

Table S10. Numbers of distinguishable structures and torsions

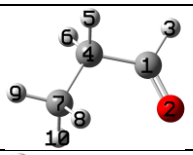
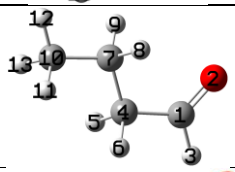
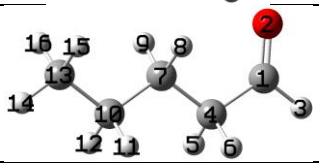
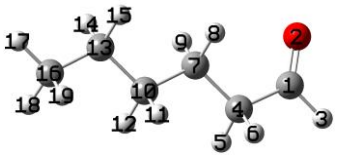
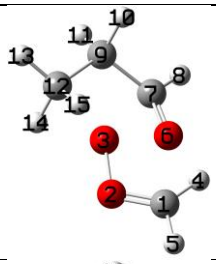
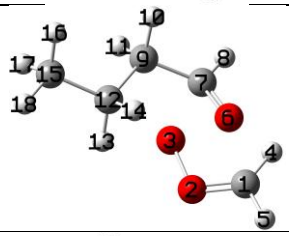
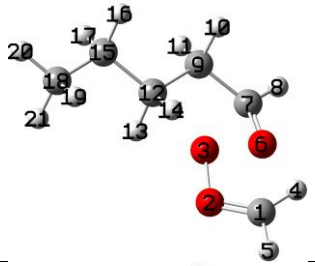
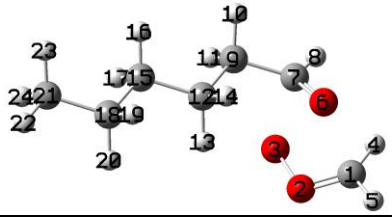
	molecule	distinguishable structures	torsions
C_2H_5CHO		2	10-7-4-1 7-4-1-2
C_3H_7CHO		4	13-10-7-4 10-7-4-1 7-4-1-2
C_4H_9CHO		12	16-13-10-7 13-10-7-4 10-7-4-1 7-4-1-2
$C_5H_{11}CHO$		35	19-16-13-10 16-13-10-7 13-10-7-4 10-7-4-1 7-4-1-2
TS3		6	15-12-9-7 12-9-7-6 9-7-2-1
TS4		18	18-15-12-9 15-12-9-7 12-9-7-6 9-7-2-1
TS5		24	21-18-15-12 18-15-12-9 15-12-9-7 12-9-7-6 9-7-2-1
TS6		79	24-21-18-15 21-18-15-12 18-15-12-9 15-12-9-7 12-9-7-6 9-7-2-1

Table S11. The enthalpy of activation at 0 K (in kcal/mol) for the transition states of CH_2OO + XCHO (X = C_2H_5/ C_3H_7/C_4H_9/C_5H_{11} reaction as calculated using various theoretical methods with the standard vibrational scale factors

Method	$\Delta H_0^{\ddagger}$	
	TS3	UD
BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ	−4.50	0.00
BE2//DF-CCSD(T)-F12b/jun-cc-pVDZ	−4.52	0.02
W3X-L//DF-CCSD(T)-F12a/jun-cc-pVDZ	−4.79	0.29
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.16	0.66
W2X//DF-CCSD(T)-F12a/cc-pVDZ	−5.19	0.69
W2X//DF-CCSD(T)-F12b/VDZ(d)	−5.20	0.70
DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.11	0.61
DF-CCSD(T)-F12a/cc-pVDZ	−6.87	2.37
DF-CCSD(T)-F12b/VDZ(d)	−7.03	2.53
M11-L/MG3S	−4.25	0.25
Method	$\Delta H_0^{\ddagger}$	
	TS4	UD
BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ	−4.63	0.00
BE2//DF-CCSD(T)-F12b/jun-cc-pVDZ	−4.64	0.01
W3X-L//DF-CCSD(T)-F12a/VDZ(d)	−4.91	0.28
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.29	0.66
W2X//DF-CCSD(T)-F12a/cc-pVDZ	−5.40	0.77
W2X//DF-CCSD(T)-F12b/VDZ(d)	−5.35	0.72
DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.29	0.66
DF-CCSD(T)-F12a/cc-pVDZ	−7.00	2.37
DF-CCSD(T)-F12b/VDZ(d)	−7.15	2.52
M11-L/MG3S	−4.33	0.30
Method	$\Delta H_0^{\ddagger}$	
	TS5	UD
BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ	−4.70	0.00
BE2//DF-CCSD(T)-F12b/jun-cc-pVDZ	−4.70	0.00
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.35	0.72
W2X//DF-CCSD(T)-F12a/cc-pVDZ	−5.46	0.83
W2X//DF-CCSD(T)-F12b/VDZ(d)	−5.41	0.78
DF-CCSD(T)-F12a/jun-cc-pVDZ	−5.38	0.75
DF-CCSD(T)-F12a/cc-pVDZ	−7.08	2.45
DF-CCSD(T)-F12b/VDZ(d)	−7.22	2.59
M11-L/MG3S	−4.37	0.33
Method	$\Delta H_0^{\ddagger}$	
	TS6	UD
BE1//DF-CCSD(T)-F12b/VDZ(d)	−4.80	0.00
BE2//DF-CCSD(T)-F12b/VDZ(d)	−4.84	0.04
W2X//DF-CCSD(T)-F12a/cc-pVDZ	−5.55	0.75
W2X//DF-CCSD(T)-F12b/VDZ(d)	−5.48	0.68
DF-CCSD(T)-F12a/cc-pVDZ	−7.16	2.36
DF-CCSD(T)-F12b/VDZ(d)	−7.22	2.42
M11-L/MG3S	−4.33	0.47

Table S12. The enthalpy of activation at 0 K (in kcal/mol) for the transition states of CH_2OO + XCHO (X = CH_2F/ CHF_2/CF_3) reaction as calculated using various theoretical methods with the standard vibrational scale factors

Method	$\Delta H_0^{\ddagger}$	
	TS7	UD
BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ	−6.21	0.00
BE2//DF-CCSD(T)-F12b/jun-cc-pVDZ	−6.24	0.03
W3X-L//DF-CCSD(T)-F12a/jun-cc-pVDZ	−6.42	0.21
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−6.88	0.67
DF-CCSD(T)-F12a/jun-cc-pVDZ	−6.83	0.62
M11-L/MG3S	−5.98	0.23
Method	$\Delta H_0^{\ddagger}$	
	TS8	UD
BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ	−7.96	0.00
BE2//DF-CCSD(T)-F12b/jun-cc-pVDZ	−7.99	0.03
W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ	−8.63	0.67
DF-CCSD(T)-F12a/jun-cc-pVDZ	−8.74	0.78
M11-L/MG3S	−8.40	0.44
Method	$\Delta H_0^{\ddagger}$	
	TS9	UD
M11-L/MG3S	−9.74	0.00

Table S13. Rate constants *k* (T, p) of the CH_2OO + HCHO as a function of temperature and pressure by TST/Eckart method with subsequent reaction.

P (bar)	200 K	220 K	240 K	260 K
0.0316	3.88E-10	2.61E-10	1.46E-10	7.65E-11
0.1	4.00E-10	2.71E-10	1.53E-10	8.14E-11
0.178	4.05E-10	2.76E-10	1.57E-10	8.38E-11
0.316	4.05E-10	2.76E-10	1.57E-10	8.39E-11
0.562	4.07E-10	2.78E-10	1.58E-10	8.48E-11
1	4.07E-10	2.78E-10	1.59E-10	8.51E-11
1.78	4.08E-10	2.79E-10	1.59E-10	8.54E-11
3.16	4.09E-10	2.80E-10	1.59E-10	8.56E-11
5.62	4.10E-10	2.80E-10	1.60E-10	8.58E-11
31.6	4.11E-10	2.81E-10	1.60E-10	8.60E-11
100	4.14E-10	2.82E-10	1.61E-10	8.64E-11
1000	4.18E-10	2.85E-10	1.62E-10	8.70E-11
P (bar)	275 K	280K	295 K	298 K
0.0316	4.70E-11	4.01E-11	2.52E-11	2.31E-11
0.1	5.06E-11	4.33E-11	2.75E-11	2.52E-11
0.178	5.24E-11	4.49E-11	2.88E-11	2.64E-11
0.316	5.24E-11	4.50E-11	2.89E-11	2.65E-11
0.562	5.31E-11	4.56E-11	2.94E-11	2.70E-11
1	5.34E-11	4.59E-11	2.95E-11	2.71E-11
1.78	5.36E-11	4.61E-11	2.97E-11	2.73E-11
3.16	5.38E-11	4.62E-11	2.98E-11	2.74E-11
5.62	5.39E-11	4.63E-11	2.99E-11	2.75E-11
31.6	5.40E-11	4.64E-11	3.00E-11	2.76E-11
100	5.42E-11	4.66E-11	3.01E-11	2.76E-11
1000	5.46E-11	4.69E-11	3.02E-11	2.78E-11
P (bar)	300 K	320 K	340 K	
0.0316	2.18E-11	1.26E-11	7.59E-12	
0.1	2.39E-11	1.39E-11	8.56E-12	
0.178	2.50E-11	1.47E-11	9.14E-12	
0.316	2.50E-11	1.47E-11	9.16E-12	
0.562	2.55E-11	1.50E-11	9.41E-12	
1	2.57E-11	1.52E-11	9.50E-12	
1.78	2.58E-11	1.53E-11	9.59E-12	
3.16	2.59E-11	1.53E-11	9.65E-12	
5.62	2.60E-11	1.54E-11	9.68E-12	
31.6	2.61E-11	1.54E-11	9.71E-12	
100	2.61E-11	1.55E-11	9.74E-12	
1000	2.63E-11	1.55E-11	9.79E-12	

Table S14. Rate constants *k* (T, p) of the $CH_2OO + CH_3CHO$ for Schame 2b as a function of temperature and pressure by TST/Eckart method.

P (Torr)	200 K	220 K	240 K	260 K
4.00	6.69E-11	2.35E-11	1.02E-11	5.11E-12
9.75	6.61E-11	2.35E-11	1.02E-11	5.12E-12
23.7	6.63E-11	2.36E-11	1.02E-11	5.13E-12
25	6.63E-11	2.36E-11	1.02E-11	5.13E-12
50	6.65E-11	2.36E-11	1.02E-11	5.14E-12
75	6.67E-11	2.37E-11	1.02E-11	5.15E-12
133.5	6.71E-11	2.38E-11	1.03E-11	5.17E-12
237	6.79E-11	2.41E-11	1.04E-11	5.21E-12
412.5	6.93E-11	2.45E-11	1.05E-11	5.27E-12
750	7.18E-11	2.52E-11	1.08E-11	5.39E-12
1335	7.54E-11	2.65E-11	1.13E-11	5.58E-12
2370	8.11E-11	2.81E-11	1.20E-11	5.91E-12
3000	8.39E-11	2.89E-11	1.25E-11	6.10E-12
4215	8.82E-11	3.03E-11	1.27E-11	6.45E-12
7500	9.49E-11	3.24E-11	1.35E-11	6.51E-12
P (Torr)	280 K	293 K	295 K	298 K
4.00	2.88E-12	1.84E-12	1.76E-12	1.65E-12
9.75	2.88E-12	1.85E-12	1.77E-12	1.65E-12
23.7	2.89E-12	1.85E-12	1.77E-12	1.65E-12
25	2.89E-12	1.85E-12	1.77E-12	1.65E-12
50	2.89E-12	1.85E-12	1.77E-12	1.66E-12
75	2.90E-12	1.86E-12	1.77E-12	1.66E-12
133.5	2.91E-12	1.86E-12	1.78E-12	1.66E-12
237	2.93E-12	1.87E-12	1.79E-12	1.67E-12
412.5	2.96E-12	1.89E-12	1.81E-12	1.69E-12
750	3.01E-12	1.92E-12	1.83E-12	1.72E-12
1335	3.11E-12	1.97E-12	1.89E-12	1.76E-12
2370	3.26E-12	2.06E-12	1.97E-12	1.84E-12
3000	3.35E-12	2.12E-12	2.02E-12	1.88E-12
4215	3.52E-12	2.21E-12	2.11E-12	1.96E-12
7500	3.93E-12	2.45E-12	2.33E-12	2.16E-12
P (Torr)	320 K	340 K		
4.00	1.06E-12	7.46E-13		
9.75	1.06E-12	7.50E-13		
23.7	1.06E-12	7.52E-13		
25	1.06E-12	7.52E-13		
50	1.06E-12	7.53E-13		
75	1.06E-12	7.54E-13		
133.5	1.07E-12	7.55E-13		
237	1.07E-12	7.58E-13		

412.5	1.08E-12	7.63E-13		
750	1.09E-12	7.72E-13		
1335	1.12E-12	7.86E-13		
2370	1.16E-12	8.10E-13		
3000	1.18E-12	8.24E-13		
4215	1.22E-12	8.49E-13		
7500	1.33E-12	9.10E-13		

Table S15. Rate constants *k* (T, p) of the $CH_2OO + CH_3CHO$ for Schame 2a as a function of temperature and pressure by TST/Eckart method.

P (Torr)	200 K	220 K	240 K	260 K
4.00	6.66E-11	2.35E-11	1.01E-11	5.08E-12
9.75	6.66E-11	2.36E-11	1.02E-11	5.09E-12
23.7	6.68E-11	2.36E-11	1.02E-11	5.10E-12
25	6.68E-11	2.36E-11	1.02E-11	5.10E-12
50	6.71E-11	2.37E-11	1.02E-11	5.12E-12
75	6.74E-11	2.38E-11	1.02E-11	5.13E-12
133.5	6.80E-11	2.40E-11	1.03E-11	5.16E-12
237	6.92E-11	2.43E-11	1.04E-11	5.21E-12
412.5	7.12E-11	2.49E-11	1.07E-11	5.31E-12
750	7.44E-11	2.60E-11	1.10E-11	5.47E-12
1335	7.93E-11	2.74E-11	1.17E-11	5.75E-12
2370	8.57E-11	2.94E-11	1.23E-11	6.21E-12
3000	8.85E-11	3.02E-11	1.26E-11	6.49E-12
4215	9.22E-11	3.14E-11	1.31E-11	6.34E-12
7500	9.61E-11	3.27E-11	1.36E-11	6.54E-12
P (Torr)	280 K	293 K	295 K	298 K
4.00	2.86E-12	2.07E-12	1.97E-12	1.84E-12
9.75	2.87E-12	2.07E-12	1.98E-12	1.84E-12
23.7	2.87E-12	2.07E-12	1.98E-12	1.85E-12
25	2.87E-12	2.07E-12	1.98E-12	1.85E-12
50	2.88E-12	2.08E-12	1.98E-12	1.85E-12
75	2.88E-12	2.08E-12	1.99E-12	1.85E-12
133.5	2.90E-12	2.09E-12	2.00E-12	1.86E-12
237	2.92E-12	2.11E-12	2.01E-12	1.88E-12
412.5	2.97E-12	2.14E-12	2.04E-12	1.90E-12
750	3.05E-12	2.19E-12	2.09E-12	1.94E-12
1335	3.18E-12	2.27E-12	2.17E-12	2.02E-12
2370	3.40E-12	2.41E-12	2.30E-12	2.14E-12
3000	3.53E-12	2.50E-12	2.37E-12	2.21E-12
4215	3.76E-12	2.65E-12	2.52E-12	2.33E-12
7500	3.54E-12	2.51E-12	2.38E-12	2.21E-12
P (Torr)	320 K	340 K		

4.00	9.96E-13	7.09E-13		
9.75	1.00E-12	7.13E-13		
23.7	1.00E-12	7.15E-13		
25	1.00E-12	7.15E-13		
50	1.00E-12	7.17E-13		
75	1.01E-12	7.18E-13		
133.5	1.01E-12	7.20E-13		
237	1.02E-12	7.24E-13		
412.5	1.03E-12	7.31E-13		
750	1.05E-12	7.42E-13		
1335	1.08E-12	7.62E-13		
2370	1.13E-12	7.93E-13		
3000	1.16E-12	8.12E-13		
4215	1.22E-12	8.44E-13		
7500	1.35E-12	9.22E-13		

Table S16. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + HCHO reaction.

T/K	k_{HL}^{TST} [a]	κ_{LL}^{SCT} [b]	Γ_{CVT}^{LL} [c]	$F_{act}^{MS-T,LL}$ [d]	$k_{1,tight}$ [e]	$k_{1,loose}$ [f]	k_1 [g]
190	2.96E-09	1.45E+00	0.92	0.511	8.02E-09	5.13E-10	4.82E-10
200	1.43E-09	1.39E+00	0.92	0.511	2.91E-09	4.99E-10	4.26E-10
210	7.46E-10	1.34E+00	0.92	0.511	1.48E-09	4.85E-10	3.65E-10
220	4.13E-10	1.30E+00	0.92	0.511	8.03E-10	4.72E-10	2.97E-10
230	2.41E-10	1.27E+00	0.92	0.511	4.61E-10	4.59E-10	2.30E-10
240	1.47E-10	1.24E+00	0.91	0.511	2.79E-10	4.46E-10	1.71E-10
250	9.40E-11	1.22E+00	0.91	0.511	1.76E-10	4.33E-10	1.25E-10
260	6.22E-11	1.20E+00	0.91	0.511	1.15E-10	4.21E-10	9.04E-11
270	4.25E-11	1.18E+00	0.91	0.511	7.80E-11	4.11E-10	6.56E-11
280	2.99E-11	1.17E+00	0.91	0.511	5.45E-11	4.02E-10	4.80E-11
290	2.16E-11	1.16E+00	0.91	0.511	3.91E-11	3.94E-10	3.56E-11
298	1.70E-11	1.15E+00	0.91	0.512	3.06E-11	3.88E-10	2.83E-11
300	1.60E-11	1.14E+00	0.91	0.512	2.88E-11	3.86E-10	2.68E-11
310	1.21E-11	1.13E+00	0.91	0.512	2.17E-11	3.82E-10	2.05E-11
320	9.31E-12	1.12E+00	0.91	0.512	1.66E-11	3.79E-10	1.59E-11
330	7.30E-12	1.12E+00	0.90	0.512	1.30E-11	3.73E-10	1.25E-11
340	5.81E-12	1.11E+00	0.90	0.512	1.03E-11	3.73E-10	1.00E-11
350	4.70E-12	1.10E+00	0.90	0.512	8.28E-12	3.67E-10	8.10E-12

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] $k_{1,tight}$ is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

[f] $k_{1,loose}$ is the rate constant from reactant CH_2OO and HCHO to C1 calculated by variable-reaction-coordinate variational transition-state theory (VRC-VTST), the data obtained by the work of Long et al. (Long et al., 2021)

[g] k_1 is high-pressure-limit rate constant, which equals $\frac{k_{1,\mathrm{loose}}k_{1,\mathrm{tight}}}{k_{1,\mathrm{loose}}+k_{1,\mathrm{tight}}}$.

Table S17. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + CH_3CHO reaction.

T/K	k_{HL}^{TST}[a]	κ_{LL}^{SCT}[b]	Γ_{CVT}^{LL}[c]	$F_{act}^{MS-T,LL}$[d]	k_2[e]
190	9.85E-11	1.42E+00	0.97	0.66	1.79E-10
200	5.34E-11	1.37E+00	0.97	0.67	9.49E-11
210	3.08E-11	1.33E+00	0.97	0.68	5.39E-11
220	1.87E-11	1.30E+00	0.97	0.69	3.24E-11
230	1.19E-11	1.27E+00	0.97	0.70	2.04E-11
240	7.90E-12	1.24E+00	0.97	0.71	1.34E-11
250	5.43E-12	1.22E+00	0.97	0.72	9.19E-12
260	3.85E-12	1.20E+00	0.96	0.73	6.49E-12
270	2.81E-12	1.19E+00	0.96	0.73	4.72E-12
280	2.10E-12	1.17E+00	0.96	0.74	3.52E-12
290	1.60E-12	1.16E+00	0.96	0.75	2.69E-12
293	1.49E-12	1.16E+00	0.96	0.75	2.49E-12
295	1.41E-12	1.15E+00	0.96	0.76	2.37E-12
298	1.31E-12	1.15E+00	0.96	0.76	2.20E-12
300	1.25E-12	1.15E+00	0.96	0.76	2.10E-12
310	9.94E-13	1.14E+00	0.96	0.77	1.67E-12
320	8.03E-13	1.13E+00	0.96	0.77	1.35E-12
330	6.58E-13	1.12E+00	0.96	0.78	1.10E-12
340	5.47E-13	1.11E+00	0.96	0.79	9.19E-13
350	4.60E-13	1.11E+00	0.96	0.80	7.74E-13

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{F_{TS}^{MS-T,M11-L/MG3S}}{F_{R}^{MS-T,M11-L/MG3S}}$.

[e] k_2 is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)F_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

Table S18. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + C_2H_5CHO reaction.

T/K	k_{HL}^{TST} [a]	κ_{LL}^{SCT} [b]	Γ_{CVT}^{LL} [c]	$F_{act}^{MS-T,LL}$ [d]	k_3 [e]
190	5.63E-11	1.36E+00	0.99	1.34	2.04E-10
200	3.08E-11	1.32E+00	0.99	1.35	1.09E-10
210	1.79E-11	1.29E+00	0.99	1.36	6.19E-11
220	1.10E-11	1.26E+00	0.99	1.37	3.73E-11
230	7.03E-12	1.23E+00	0.99	1.38	2.35E-11
240	4.69E-12	1.21E+00	0.99	1.38	1.55E-11
250	3.24E-12	1.19E+00	0.99	1.39	1.06E-11
260	2.31E-12	1.18E+00	0.99	1.39	7.48E-12
270	1.69E-12	1.16E+00	0.98	1.40	5.43E-12
280	1.27E-12	1.15E+00	0.98	1.40	4.05E-12
290	9.77E-13	1.14E+00	0.98	1.41	3.08E-12
298	8.02E-13	1.13E+00	0.98	1.41	2.52E-12
300	7.65E-13	1.13E+00	0.98	1.41	2.40E-12
310	6.10E-13	1.12E+00	0.98	1.42	1.90E-12
320	4.94E-13	1.11E+00	0.98	1.42	1.53E-12
330	4.06E-13	1.11E+00	0.98	1.42	1.25E-12
340	3.38E-13	1.10E+00	0.98	1.42	1.04E-12
350	2.85E-13	1.09E+00	0.98	1.43	8.73E-13

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] k_3 is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

Table S19. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + C_3H_7CHO reaction.

T/K	k_{HL}^{TST}[a]	κ_{LL}^{SCT}[b]	Γ_{CVT}^{LL}[c]	$F_{act}^{MS-T,LL}$[d]	k_4[e]
190	7.07E-11	1.38E+00	0.99	1.14	2.20E-10
200	3.82E-11	1.33E+00	0.99	1.18	1.19E-10
210	2.20E-11	1.30E+00	0.99	1.22	6.89E-11
220	1.33E-11	1.26E+00	0.99	1.26	4.21E-11
230	8.47E-12	1.24E+00	0.99	1.29	2.70E-11
240	5.61E-12	1.22E+00	0.99	1.33	1.81E-11
250	3.85E-12	1.20E+00	0.99	1.37	1.25E-11
260	2.72E-12	1.18E+00	0.99	1.40	8.98E-12
270	1.98E-12	1.17E+00	0.99	1.44	6.62E-12
280	1.48E-12	1.15E+00	1.00	1.47	5.00E-12
290	1.13E-12	1.14E+00	1.00	1.50	3.86E-12
298	9.25E-13	1.13E+00	1.00	1.53	3.19E-12
300	8.81E-13	1.13E+00	1.00	1.54	3.05E-12
310	6.99E-13	1.12E+00	1.00	1.57	2.45E-12
320	5.64E-13	1.11E+00	1.00	1.60	2.00E-12
330	4.62E-13	1.11E+00	1.00	1.63	1.66E-12
340	3.83E-13	1.10E+00	1.00	1.66	1.39E-12
350	3.22E-13	1.09E+00	1.00	1.68	1.18E-12

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] k_4 is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

Table S20. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH2OO + C_4H_9CHO reaction.

T/K	k_{HL}^{TST}[a]	κ_{LL}^{SCT}[b]	Γ_{CVT}^{LL}[c]	$F_{act}^{MS-T,LL}$[d]	k_5[e]
190	8.30E-11	1.35E+00	0.99	0.93	2.08E-10
200	4.46E-11	1.31E+00	0.99	0.95	1.10E-10
210	2.55E-11	1.28E+00	0.99	0.96	6.21E-11
220	1.54E-11	1.25E+00	0.99	0.97	3.71E-11
230	9.76E-12	1.22E+00	0.99	0.99	2.33E-11
240	6.43E-12	1.20E+00	0.99	1.00	1.53E-11
250	4.40E-12	1.18E+00	0.99	1.01	1.04E-11
260	3.10E-12	1.17E+00	0.99	0.97	6.95E-12
270	2.25E-12	1.16E+00	0.99	0.98	5.03E-12
280	1.68E-12	1.14E+00	0.99	0.99	3.74E-12
290	1.28E-12	1.13E+00	0.99	0.99	2.85E-12
298	1.04E-12	1.12E+00	0.99	1.01	2.34E-12
300	9.92E-13	1.12E+00	0.99	1.04	2.28E-12
310	7.85E-13	1.11E+00	0.99	1.01	1.75E-12
320	6.32E-13	1.11E+00	0.99	1.02	1.41E-12
330	5.16E-13	1.10E+00	0.99	1.02	1.15E-12
340	4.27E-13	1.09E+00	0.99	1.03	9.51E-13
350	3.58E-13	1.09E+00	0.99	1.03	7.97E-13

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] k_5 is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

Table S21. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + $C_5H_{11}CHO$ reaction.

T/K	k_{HL}^{TST} [a]	κ_{LL}^{SCT} [b]	Γ_{CVT}^{LL} [c]	$F_{act}^{MS-T,LL}$ [d]	k_6 [e]
190	1.16E-10	1.43E+00	0.90	1.37	4.09E-10
200	6.18E-11	1.36E+00	0.90	1.41	2.14E-10
210	3.50E-11	1.31E+00	0.90	1.46	1.21E-10
220	2.09E-11	1.27E+00	0.90	1.50	7.19E-11
230	1.31E-11	1.24E+00	0.90	1.54	4.51E-11
240	8.59E-12	1.21E+00	0.89	1.58	2.95E-11
250	5.83E-12	1.19E+00	0.89	1.62	2.01E-11
260	4.08E-12	1.17E+00	0.89	1.54	1.31E-11
270	2.95E-12	1.16E+00	0.89	1.57	9.53E-12
280	2.18E-12	1.14E+00	0.89	1.60	7.09E-12
290	1.65E-12	1.13E+00	0.88	1.63	5.40E-12
298	1.34E-12	1.12E+00	0.88	1.67	4.46E-12
300	1.28E-12	1.12E+00	0.88	1.74	4.41E-12
310	1.01E-12	1.11E+00	0.88	1.68	3.32E-12
320	8.08E-13	1.10E+00	0.88	1.71	2.67E-12
330	6.57E-13	1.10E+00	0.87	1.73	2.18E-12
340	5.42E-13	1.09E+00	0.87	1.75	1.80E-12
350	4.53E-13	1.08E+00	0.87	1.77	1.51E-12

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] k_6 is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

Table S22. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + CH_2FCHO reaction.

T/K	k_{HL}^{TST}	κ_{LL}^{SCT}	Γ_{CVT}^{LL}	$F_{act}^{MS-T,LL}$	$k_{7,\mathrm{tight}}$	$k_{7,\mathrm{loose}}$	k_7
190	2.53E-09	1.36E+00	0.96	0.76	5.05E-09	5.70E-10	5.12E-10
200	1.08E-09	1.32E+00	0.96	0.79	2.16E-09	5.37E-10	4.30E-10
210	5.03E-10	1.29E+00	0.96	0.81	1.00E-09	5.10E-10	3.38E-10
220	2.51E-10	1.26E+00	0.96	0.83	5.06E-10	4.86E-10	2.48E-10
230	1.34E-10	1.23E+00	0.96	0.86	2.72E-10	4.66E-10	1.72E-10
240	7.51E-11	1.21E+00	0.96	0.89	1.55E-10	4.49E-10	1.15E-10
250	4.43E-11	1.19E+00	0.96	0.92	9.28E-11	4.34E-10	7.65E-11
260	2.73E-11	1.18E+00	0.96	0.94	5.82E-11	4.22E-10	5.11E-11
270	1.75E-11	1.16E+00	0.96	0.97	3.79E-11	4.10E-10	3.47E-11
280	1.16E-11	1.15E+00	0.96	1.00	2.55E-11	4.00E-10	2.40E-11
290	7.89E-12	1.14E+00	0.96	1.03	1.78E-11	3.92E-10	1.70E-11
298	5.93E-12	1.13E+00	0.95	1.06	1.36E-11	3.85E-10	1.31E-11
300	5.54E-12	1.13E+00	0.95	1.07	1.27E-11	3.84E-10	1.23E-11
310	3.98E-12	1.12E+00	0.95	1.10	9.35E-12	3.77E-10	9.13E-12
320	2.93E-12	1.11E+00	0.95	1.13	7.03E-12	3.71E-10	6.90E-12
330	2.20E-12	1.11E+00	0.95	1.17	5.39E-12	3.65E-10	5.31E-12
340	1.68E-12	1.10E+00	0.95	1.20	4.21E-12	3.60E-10	4.17E-12
350	1.31E-12	1.09E+00	0.95	1.23	3.35E-12	3.55E-10	3.32E-12

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] $k_{7,\mathrm{tight}}$ is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

[f] $k_{7,\mathrm{loose}}$ is the rate constant from reactant CH_2OO and HCHO to C1 calculated by variable-reaction-coordinate variational transition-state theory (VRC-VTST).

[g] k_7 is high-pressure-limit rate constant, which equals $\frac{k_{7,\mathrm{loose}}k_{7,\mathrm{tight}}}{k_{7,\mathrm{loose}}+k_{7,\mathrm{tight}}}$.

Table S23. The high-pressure limiting rate constants (cm3 molecule^{-1} s^{-1}) of the CH_2OO + CHF_2CHO reaction.

T/K	k_{HL}^{TST}	κ_{LL}^{SCT}	Γ_{CVT}^{LL}	$F_{act}^{MS-T,LL}$	$k_{8,\mathrm{tight}}$	$k_{8,\mathrm{loose}}$	k_8
190	2.04E-07	1.24E+00	0.92	1.55	7.22E-07	4.63E-10	4.62E-10
200	7.01E-08	1.21E+00	0.92	1.60	2.50E-07	4.52E-10	4.51E-10
210	2.68E-08	1.19E+00	0.92	1.64	9.64E-08	4.35E-10	4.33E-10
220	1.12E-08	1.17E+00	0.92	1.68	4.07E-08	4.20E-10	4.16E-10
230	5.07E-09	1.16E+00	0.92	1.72	1.86E-08	4.08E-10	3.99E-10
240	2.46E-09	1.14E+00	0.92	1.76	9.15E-09	3.97E-10	3.81E-10
250	1.27E-09	1.13E+00	0.92	1.81	4.78E-09	3.88E-10	3.59E-10
260	6.89E-10	1.12E+00	0.92	1.85	2.63E-09	3.75E-10	3.28E-10
270	3.92E-10	1.11E+00	0.92	1.89	1.52E-09	3.61E-10	2.92E-10
280	2.33E-10	1.10E+00	0.92	1.93	9.17E-10	3.48E-10	2.52E-10
290	1.44E-10	1.10E+00	0.92	1.97	5.74E-10	3.38E-10	2.13E-10
298	1.01E-10	1.09E+00	0.92	2.01	4.05E-10	3.30E-10	1.82E-10
300	9.22E-11	1.09E+00	0.92	2.02	3.72E-10	3.28E-10	1.74E-10
310	6.08E-11	1.08E+00	0.92	2.06	2.49E-10	3.19E-10	1.40E-10
320	4.12E-11	1.08E+00	0.92	2.10	1.71E-10	3.12E-10	1.10E-10
330	2.87E-11	1.07E+00	0.92	2.14	1.21E-10	3.05E-10	8.65E-11
340	2.04E-11	1.07E+00	0.92	2.18	8.71E-11	2.99E-10	6.74E-11
350	1.48E-11	1.06E+00	0.92	2.22	6.42E-11	2.93E-10	5.27E-11

[a] k_{HL}^{TST} is the high-level (HL) calculation by conventional transition state theory without a transmission coefficient.

[b] κ_{LL}^{SCT} is the tunneling transmission coefficient calculated by the small-curvature tunneling at LL level.

[c] Γ_{CVT}^{LL} is the recrossing transmission coefficient, which equals $\frac{k_{LL}^{TST}}{k_{LL}^{CVT}}$.

[d] $F_{act}^{MS-T,LL}$ is the multi-structure anharmonic factor, which equals $\frac{\mathrm{F_{TS}^{MS-T,M11-L/MG3S}}}{\mathrm{F_{R}^{MS-T,M11-L/MG3S}}}$.

[e] $k_{8,\mathrm{tight}}$ is calculated by the dual-level strategy, which equals

$k_{\mathrm{HL}}^{\mathrm{TST}}(T)\kappa_{\mathrm{LL}}(\mathrm{T})\Gamma_{\mathrm{LL}}(T)\mathrm{F}_{\mathrm{fwd}}^{\mathrm{MS-T,LL}}(\mathrm{T})$.

[f] $k_{8,\mathrm{loose}}$ is the rate constant from reactant CH_2OO and HCHO to C1 calculated by variable-reaction-coordinate variational transition-state theory (VRC-VTST).

[g] k_8 is high-pressure-limit rate constant, which equals $\frac{k_{8,\mathrm{loose}}k_{8,\mathrm{tight}}}{k_{8,\mathrm{loose}}+k_{8,\mathrm{tight}}}$.

Table S24. The high-pressure limiting rate constants (cm^3 $molecule^{-1}$ s^{-1}) of the CH_2OO + CF_3CHO reaction.

T/K	k_9
190	7.73E-10
200	7.40E-10
210	7.11E-10
220	6.88E-10
230	6.68E-10
240	6.52E-10
250	6.38E-10
260	6.26E-10
270	6.15E-10
280	6.07E-10
290	5.99E-10
298	5.94E-10
300	5.93E-10
310	5.88E-10
320	5.83E-10
330	5.79E-10
340	5.76E-10
350	5.74E-10

Table S25. Fitting Parameters for all aldehydes.

	A	n	E	T_0
HCHO	1.21×10^{-33}	27.94	-41.78	-50.70
CH_3CHO	6.87×10^{-16}	1.51	-4.12	47.25
C_2H_5CHO	1.36×10^{-13}	-4.05	-0.50	-137.77
C_3H_7CHO	1.19×10^{-15}	1.62	-4.07	41.13
C_4H_9CHO	2.93×10^{-16}	2.23	-4.33	66.75
$C_5H_{11}CHO$	6.79×10^{-16}	2.03	-4.30	61.81
CH_2FCHO	2.80×10^{-41}	39.97	-54.76	-48.01
CHF_2CHO	4.14×10^{-18}	-5.74	-20.16	-149.52
CF_3CHO	8.08×10^{-10}	-0.03	0.58	-166.04

Table S26. The rate constant for the conversion of C2b.

T	$k_{C2b\text{-}TS2b}$	$k_{C2b\text{-}TSISO}$
190	6.82E+08	3.78E+10
200	9.03E+08	5.56E+10
210	1.16E+09	7.88E+10
220	1.45E+09	1.08E+11
230	1.79E+09	1.45E+11
240	2.15E+09	1.90E+11
250	2.55E+09	2.44E+11
260	2.98E+09	3.07E+11
270	3.44E+09	3.80E+11
280	3.92E+09	4.63E+11
290	4.43E+09	5.57E+11
298	4.85E+09	6.41E+11
300	4.96E+09	6.63E+11
310	5.51E+09	7.80E+11
320	6.07E+09	9.09E+11
330	6.65E+09	1.05E+12
340	7.25E+09	1.20E+12
350	7.85E+09	1.37E+12

Table S27. Rate ratio v_i between the reaction R2-R4 and OH + CH_3CHO/C_2H_5CHO with different concentrations of OH and CH_2OO at different heights from different region in GEOS-Chem

Height	T/K	P/mBar	$[CH_2OO]^a$	$[OH]^a$	$[CH_2OO]/[OH]^a$	$v_2{}^a$	$v_3{}^b$
Gansu, China							
1	290.2	1013	2.18	8.77×10^3	2.48×10^{-4}	4.22E-05	4.16E-05
5	250.5	495.9	6.99	2.26×10^4	3.09×10^{-4}	1.52E-04	1.71E-04
10	215.6	242.8	0.85	2.42×10^4	3.51×10^{-5}	6.24E-05	8.31E-05
Russia							
1	290.2	1013	8.93×10^2	5.88×10^4	1.52×10^{-2}	2.58E-03	2.54E-03
5	250.5	495.9	2.25×10^2	3.52×10^4	6.39×10^{-3}	3.14E-03	3.54E-03
10	215.6	242.8	2.69	8.33×10^4	3.23×10^{-5}	5.73E-05	7.64E-05
Arctic							
1	290.2	1013	1.96×10^3	1.71×10^5	1.15×10^{-2}	1.95E-03	1.92E-03
5	250.5	495.9	3.55×10^1	6.89×10^4	5.16×10^{-4}	2.53E-04	2.86E-04
10	215.6	242.8	0.894	4.68×10^5	1.91×10^{-6}	3.39E-06	4.52E-06
Indonesia							
1	290.2	1013	2.18×10^2	6.90×10^4	3.16×10^{-3}	5.36E-04	5.29E-04
5	250.5	495.9	8.08×10^1	1.38×10^4	5.85×10^{-3}	2.87E-03	3.24E-03
10	215.6	242.8	207.51	8.19×10^3	2.53×10^{-2}	4.50E-02	5.99E-02

[a] the product of rate ratio and concentration ratio of reaction R2.

[b] the product of rate ratio and concentration ratio of reaction R3.

Table S28. Rate ratio v_i between the reaction R4-R5 and OH + C_3H_7CHO/C_4H_9CHO with different concentrations of OH and CH_2OO at different heights from different region in GEOS-Chem

Height	T/K	P/mBar	$[CH_2OO]^a$	$[OH]^a$	$[CH_2OO]/[OH]^a$	$v_4{}^a$	$v_5{}^b$
Gansu, China							
1	290.2	1013	2.18	8.77×10^3	2.48×10^{-4}	3.90E-05	2.64E-05
5	250.5	495.9	6.99	2.26×10^4	3.09×10^{-4}	1.55E-04	1.15E-04
10	215.6	242.8	0.85	2.42×10^4	3.51×10^{-5}	7.43E-05	6.02E-05
Russia							
1	290.2	1013	8.93×10^2	5.88×10^4	1.52×10^{-2}	2.39E-03	1.61E-03
5	250.5	495.9	2.25×10^2	3.52×10^4	6.39×10^{-3}	3.21E-03	2.37E-03
10	215.6	242.8	2.69	8.33×10^4	3.23×10^{-5}	6.83E-05	5.54E-05
Arctic							
1	290.2	1013	1.96×10^3	1.71×10^5	1.15×10^{-2}	1.80E-03	1.22E-03
5	250.5	495.9	3.55×10^1	6.89×10^4	5.16×10^{-4}	2.59E-04	1.91E-04
10	215.6	242.8	0.894	4.68×10^5	1.91×10^{-6}	4.04E-06	3.27E-06
Indonesia							
1	290.2	1013	2.18×10^2	6.90×10^4	3.16×10^{-3}	4.96E-04	3.35E-04
5	250.5	495.9	8.08×10^1	1.38×10^4	5.85×10^{-3}	2.94E-03	2.17E-03
10	215.6	242.8	207.51	8.19×10^3	2.53×10^{-2}	5.36E-02	4.34E-02

[a] the product of rate ratio and concentration ratio of reaction R4

[b] the product of rate ratio and concentration ratio of reaction R5

Table S29. Rate ratio v_i between the reaction R6-R7 and OH + C_4H_9CHO/$C_5H_{11}CHO$ with different concentrations of OH and CH_2OO at different heights from different region in GEOS-Chem

Height	T/K	P/mBar	$[CH_2OO]^a$	$[OH]^a$	$[CH_2OO]/[OH]^a$	$v_6{}^a$	$v_7{}^b$
Gansu, China							
1	290.2	1013	2.18	8.77×10^3	2.48×10^{-4}	4.72E-05	1.70E-03
5	250.5	495.9	6.99	2.26×10^4	3.09×10^{-4}	2.07E-04	9.31E-03
10	215.6	242.8	0.85	2.42×10^4	3.51×10^{-5}	1.10E-04	3.98E-03
Russia							
1	290.2	1013	8.93×10^2	5.88×10^4	1.52×10^{-2}	2.88E-03	1.04E-01
5	250.5	495.9	2.25×10^2	3.52×10^4	6.39×10^{-3}	4.27E-03	1.93E-01
10	215.6	242.8	2.69	8.33×10^4	3.23×10^{-5}	1.01E-04	3.66E-03
Arctic							
1	290.2	1013	1.96×10^3	1.71×10^5	1.15×10^{-2}	2.18E-03	7.86E-02
5	250.5	495.9	3.55×10^1	6.89×10^4	5.16×10^{-4}	3.44E-04	1.55E-02
10	215.6	242.8	0.894	4.68×10^5	1.91×10^{-6}	5.97E-06	2.16E-04
Indonesia							
1	290.2	1013	2.18×10^2	6.90×10^4	3.16×10^{-3}	5.99E-04	2.16E-02
5	250.5	495.9	8.08×10^1	1.38×10^4	5.85×10^{-3}	3.91E-03	1.76E-01
10	215.6	242.8	207.51	8.19×10^3	2.53×10^{-2}	7.92E-02	2.87E+00

[a] the product of rate ratio and concentration ratio of reaction R6.

[b] the product of rate ratio and concentration ratio of reaction R7.

Table S30. The fitting rate constants of reactions in the GEOS-Chem.

Reaction	Rate
HCHO + CH_2OO = HCHO + HCOOH	$3.47\times 10^{-6}(300/T)^{-20.8}\exp(-3492.36/T)$
ALD2 + CH_2OO = ACTA + CH_2O	$1.44\times 10^{-16}(300/T)^{-2.42}\exp(2879.01/T)$

Table S31. Absolute energies (Hartree) and the Cartesian coordinates (Å) of the optimized geometries calculated by M11-L/MG3S.

species	Cartesian coordinates			
CH_2OO	C	1.04396000	0.19587400	0.00000000
	O	-0.00960700	-0.45046800	0.00000000
	O	-1.14305300	0.19299600	0.00000000
	H	1.00387900	1.28953700	0.00000000
	H	1.95364300	-0.40500300	-0.00000100
HCHO	O	0.00000000	0.00000000	0.66285600
	C	0.00000000	0.00000000	-0.51031800
	H	0.00000000	0.94465300	-1.12046900
	H	0.00000000	-0.94465300	-1.12046900
C	C	1.11477600	-0.91532000	0.22752100
	O	1.18444100	0.15003800	-0.38744800
	O	0.61155600	1.19828200	0.18849400
	H	0.68485400	-0.94239600	1.23157000
	H	1.54042600	-1.77681500	-0.29207000
	O	-1.32203900	-0.81598900	-0.09680800
	C	-1.54835000	0.34827000	-0.00310400
	H	-1.66378900	1.01206400	-0.89472100
	H	-1.75171600	0.85078700	0.97481200
TS	C	0.95615400	-0.87487200	0.28938300
	O	1.13473400	0.15210800	-0.38038900
	O	0.47517800	1.20832700	0.12322200
	H	0.59165000	-0.80576300	1.31588000
	H	1.35262400	-1.79456800	-0.14898100
	O	-1.11677700	-0.82571700	-0.21772500
	C	-1.38925600	0.31504300	0.07627400
	H	-1.73284900	1.04247700	-0.69114600
	H	-1.55789400	0.63908400	1.12944300
P	C	1.07975400	0.30692500	-0.13360000
	O	0.64058000	-0.91620200	0.30138100
	O	-0.64058700	-0.91619800	-0.30138300
	H	1.41279900	0.27194400	-1.19103900
	H	1.91051600	0.60830300	0.52538800
	O	0.00000300	1.15194400	-0.00000200
	C	-1.07975200	0.30693000	0.13360300
	H	-1.41278800	0.27194800	1.19104500
	H	-1.91051500	0.60831600	-0.52537700
TS11	C	1.14125400	0.27316500	0.22422300
	O	1.01202700	-0.82733200	-0.35895900
	O	-0.86028800	-0.90281300	0.30378400
	H	1.85421600	0.97843400	-0.25944800
	H	1.24591100	0.30841600	1.33351500
	O	-0.16852000	1.13965000	0.00701800
	C	-1.04723800	0.24817100	-0.23676500
	H	-1.92234600	-0.02716500	0.58275000
	H	-1.60762700	0.33626200	-1.19630500
HCOOH	O	1.09271100	-0.09062500	0.00000000
	O	-1.11319600	-0.25603700	0.00000000
	C	-0.12835400	0.38709500	0.00000000

	H	1.01707900	-1.04748000	0.00000000
	H	-0.08307100	1.49820800	0.00000000
TS21	C	0.00000000	1.10650500	0.27278600
	O	0.56011000	0.88852200	-0.87590500
	O	-0.56011000	-0.88852200	-0.87590500
	H	-1.03331700	1.52052300	0.19200700
	H	0.59712400	1.90376100	0.77850600
	O	0.00000000	0.00000000	1.10000200
	C	0.00000000	-1.10650500	0.27278600
	H	1.03331700	-1.52052300	0.19200700
	H	-0.59712400	-1.90376100	0.77850600
P21	C	-0.88991300	0.32565800	0.00000100
	O	-2.13161400	0.04532700	0.00000100
	O	1.61017800	0.79453700	-0.00000200
	H	-0.63250200	1.00682700	0.86106700
	H	-0.63251000	1.00682900	-0.86106700
	O	-0.05370000	-0.76510900	-0.00000500
	C	1.28254500	-0.43567400	0.00000400
	H	1.75515600	-0.97580100	0.86896000
	H	1.75515900	-0.97579900	-0.86895300
TS22	C	0.98867700	0.30262000	-0.29468500
	O	-0.94951300	-0.96454300	-0.28394200
	H	0.47258600	-0.20971200	-1.25149800
	O	-0.08049800	1.06362100	0.09024600
	C	-1.16471400	0.17893600	0.19097300
	H	-1.51815200	0.15464100	1.26461600
	H	-2.00083900	0.75002700	-0.30213300
	O	1.32013200	-0.66253000	0.40454900
	H	1.78165500	0.92332300	-0.77553400
P22	C	-1.08496400	-0.11395400	0.28407900
	O	-2.16761800	-0.23706800	-0.13986300
	O	1.77467600	-0.66826400	-0.04925300
	H	-0.73539800	-0.50365500	1.27511700
	H	1.93957100	-0.72172300	-0.98674600
	O	-0.13057900	0.53142300	-0.36699100
	C	1.13203400	0.49147400	0.21749200
	H	1.64867900	1.38716200	-0.16410500
	H	1.05289700	0.56436700	1.31516000
TS23	C	-1.21988500	0.23617800	-0.06612700
	O	-1.02655200	-0.97308500	0.16176200
	O	1.25198400	-0.74794300	-0.27304700
	H	-2.27242900	0.55029400	-0.23527600
	H	0.09499000	-1.10552100	0.04176900
	O	-0.35486500	1.10799600	-0.11671100
	C	1.25756400	0.38737900	0.22389500
	H	1.86286900	1.18496000	-0.24856200
	H	1.12395300	0.53317900	1.31942900
CH3CHO	O	1.21610700	-0.27158800	0.00000100
	C	0.23611100	0.38457100	-0.00000300
	H	0.29245900	1.51316100	0.00000200
	C	-1.14901800	-0.14641400	-0.00000400
	H	-1.69085600	0.23491300	0.87502800

	H	-1.69096500	0.23511200	-0.87487800
	H	-1.16205500	-1.23942300	-0.00011400
C1	C	1.37494900	-1.04280700	0.20839600
	O	1.75971300	-0.06338500	-0.42992200
	O	1.76093000	1.11189300	0.18410100
	H	1.07953200	-0.92678100	1.25516300
	H	1.36314400	-1.98633000	-0.33913100
	O	-1.28670100	-1.17373000	0.03106000
	C	-1.98148400	-0.21720700	-0.05719700
	H	-3.09215900	-0.34469100	-0.20675700
	C	-1.53498600	1.18798900	0.00878700
	H	-1.81908400	1.69432100	-0.92371100
	H	-2.09792500	1.70557600	0.79699200
	H	-0.45592600	1.29183200	0.17561600
TS1	C	1.66435700	-0.83741100	0.40156200
	O	1.74387500	0.07235800	-0.42369400
	O	1.33776500	1.27452400	-0.06217000
	H	1.28062500	-0.62972500	1.40435000
	H	1.98243300	-1.81848000	0.04562900
	O	-0.99051500	-1.24041100	-0.00717900
	C	-1.79845500	-0.41429100	-0.26815500
	C	-1.82865700	0.96441800	0.25991300
	H	-0.98986500	1.16463200	0.93102300
	H	-2.64372200	-0.65644600	-0.97594500
	H	-1.79045500	1.67141900	-0.57864200
	H	-2.79148800	1.14053400	0.75800400
C2	C	-1.68195000	0.57254700	0.54531400
	O	-1.63032200	-0.32423800	-0.29704300
	O	-0.69358100	-1.24426200	-0.13051600
	H	-1.02161900	0.54527500	1.41573200
	H	-2.42844300	1.34575200	0.35150200
	O	0.60108500	1.29439500	-0.23800200
	C	1.17947900	0.28386300	-0.49433300
	C	2.03897600	-0.46030500	0.45660700
	H	1.86763700	-1.53778400	0.37260100
	H	3.09068800	-0.28097200	0.19179100
	H	1.87580700	-0.12812500	1.48611400
	H	1.17944000	-0.12793300	-1.53877000
TS2	C	-1.38368400	0.53733600	0.61227500
	O	-1.52412100	-0.38581200	-0.20567200
	O	-0.47327200	-1.22774000	-0.17041500
	H	-0.72360800	0.41191300	1.47208400
	H	-2.10944000	1.35121900	0.53143200
	O	0.29394800	1.22573500	-0.39155500
	C	0.95616600	0.21147300	-0.53180600
	C	1.90427800	-0.28938600	0.49302400
	H	1.57105000	-0.03205300	1.50396000
	H	2.04723800	-1.37108600	0.41669300
	H	2.87954100	0.19145900	0.33100500
	H	1.10221600	-0.20545200	-1.55500100
P1	C	-1.34731400	0.59240500	0.23684500
	O	-1.34860800	-0.72168500	-0.15951500

	O	-0.03105500	-1.06941400	0.20562200
	H	-1.48975400	0.69109900	1.33282900
	H	-2.16856100	1.09389800	-0.30297500
	O	-0.11775400	1.08545600	-0.12885700
	C	0.65008800	-0.03631300	-0.40142000
	H	0.67981700	-0.19949000	-1.50156800
	C	2.01121700	0.06949100	0.18743200
	H	2.59387600	-0.83198500	-0.02327500
	H	2.53428100	0.92373100	-0.25031000
	H	1.94572400	0.21438700	1.27015500
C2H5CHO	C	-0.98140800	-0.22258000	0.00000000
	O	-0.69466500	-1.36770700	0.00000000
	H	-2.06076200	0.11104500	0.00000000
	C	0.00000000	0.89723800	0.00000000
	H	-0.24467100	1.53544300	-0.86609100
	H	-0.24467100	1.53544300	0.86609100
	C	1.42892300	0.45438100	0.00000000
	H	1.65338100	-0.16065000	-0.87822600
	H	2.11557100	1.30679500	0.00000000
	H	1.65338100	-0.16065000	0.87822600
C3	C	2.13460200	0.32174600	0.47874500
	O	1.57466000	-0.74948900	0.24608200
	O	1.01376800	-0.88355300	-0.94698700
	H	2.20608600	1.08301500	-0.30204300
	H	2.54615900	0.41973700	1.48556500
	O	-0.14728900	1.38278000	0.36740300
	C	-0.68552600	0.89740500	-0.57920100
	H	-0.44702000	1.23976800	-1.62281200
	C	-1.78794500	-0.09943700	-0.49523300
	H	-2.70282200	0.44526600	-0.79175700
	H	-1.63396400	-0.84024400	-1.29170100
	C	-1.93023100	-0.72875500	0.85442400
	H	-2.06611400	0.02568100	1.63696600
	H	-2.78437100	-1.41276200	0.89142700
	H	-1.03246100	-1.30412800	1.10994900
TS3	C	-1.98093700	0.32827300	-0.33878100
	O	-1.46410700	-0.79969400	-0.33947900
	O	-0.75172000	-1.00484800	0.79332600
	H	-2.15087000	0.85015800	0.60591600
	H	-2.45490200	0.63027400	-1.27724300
	O	-0.14392700	1.23352400	-0.38011500
	C	0.39875600	0.75681400	0.59967800
	H	0.06235600	1.03101900	1.62874500
	C	1.72844100	0.09242600	0.52244700
	H	2.46996000	0.87571400	0.76291200
	H	1.79991900	-0.63322700	1.34331400
	C	2.00751200	-0.52796800	-0.81114000
	H	3.00151200	-0.98646300	-0.83705600
	H	1.27087400	-1.30875400	-1.03298900
	H	1.95654500	0.21214500	-1.61668000
P3	C	1.88658300	-0.21047400	-0.16847000
	O	1.21844000	0.92691200	-0.53121200

	O	0.30398500	0.97760900	0.54873100
	H	2.57681400	-0.01935800	0.67937300
	H	2.44181600	-0.56883700	-1.04976500
	O	0.90589800	-1.10341700	0.18665000
	C	-0.18625300	-0.32052600	0.52019200
	C	-1.30753200	-0.51618800	-0.45630700
	H	-0.94037900	-0.20673500	-1.44544800
	H	-1.50379900	-1.59557300	-0.52436800
	H	-0.51412100	-0.52070000	1.56172800
	C	-2.53898100	0.24130300	-0.06157300
	H	-2.34173700	1.31803100	0.00454800
	H	-3.35228000	0.10099200	-0.78086200
	H	-2.91580200	-0.08134600	0.91838600
C3H7CHO	C	-1.54479400	0.39266800	0.00000000
	O	-1.98112000	-0.70447300	-0.00000300
	H	-2.22721000	1.29319000	0.00000200
	C	-0.09516800	0.72878600	0.00000200
	H	0.08463300	1.39031900	-0.86642700
	H	0.08463200	1.39031400	0.86643400
	C	0.82331000	-0.45643800	-0.00000100
	H	0.59306000	-1.08747600	0.87097700
	H	0.59306100	-1.08747200	-0.87098200
	C	2.27149300	-0.06482200	0.00000100
	H	2.52890200	0.53672300	0.88217400
	H	2.93393200	-0.93771000	0.00000000
	H	2.52890400	0.53672700	-0.88216800
C4	C	2.38889500	0.08066600	-0.63180800
	O	1.80201000	0.82458800	0.15444200
	O	1.33377300	0.27965600	1.26541000
	H	2.55384400	-0.96862100	-0.37417900
	H	2.72464000	0.55609900	-1.55577000
	O	0.14482100	-1.11869400	-1.01139000
	C	-0.25878900	-1.32544700	0.09040600
	H	0.26302400	-2.04879700	0.77480100
	C	-1.51894800	-0.76682000	0.65132600
	H	-2.15695200	-1.64326900	0.86169400
	H	-1.28131100	-0.35716400	1.64575700
	C	-2.22471700	0.23348700	-0.22099500
	H	-2.35117900	-0.19512300	-1.22697400
	H	-3.24220500	0.38303900	0.16951500
	C	-1.51618100	1.55515800	-0.31372200
	H	-0.54438900	1.45855100	-0.80975300
	H	-2.10175800	2.28572600	-0.88411200
	H	-1.33011200	1.98289500	0.68008700
TS4	C	-2.43214200	-0.08663000	-0.51302900
	O	-1.72582700	-1.05633700	-0.19637100
	O	-1.12321300	-0.84511700	0.99771100
	H	-2.80057400	0.59493400	0.25740900
	H	-2.84173500	-0.11288100	-1.52699100
	O	-0.79587300	1.13514200	-0.65773800
	C	-0.29450200	1.02285500	0.44594000
	H	-0.79697300	1.45069700	1.34688400

	C	1.13237100	0.64805500	0.63176700
	H	1.69037300	1.59864600	0.72762000
	H	1.24001700	0.15422400	1.60824500
	C	1.69631500	-0.18796100	-0.47968700
	H	1.08502700	-1.09814100	-0.57361500
	H	1.57785800	0.34730900	-1.43265800
	C	3.13562100	-0.54412100	-0.25125800
	H	3.76833800	0.35082500	-0.17539900
	H	3.26927700	-1.10992200	0.68043400
	H	3.54172400	-1.15838700	-1.06313900
P4	C	-2.33757200	0.20148600	-0.36576300
	O	-1.62320800	-0.93987600	-0.60814800
	O	-0.87433200	-0.96895400	0.59317300
	H	-3.14315500	0.02249300	0.37642200
	H	-2.75974000	0.54273600	-1.32431200
	O	-1.41938300	1.10363000	0.11159300
	C	-0.38568800	0.33006200	0.61314200
	C	0.86420900	0.51266600	-0.19330000
	H	0.65220200	0.17520400	-1.21958300
	H	1.06676400	1.59244100	-0.26147300
	H	-0.21372400	0.54970600	1.68748000
	C	2.04281200	-0.21728200	0.38445400
	H	1.79649000	-1.28661400	0.47623300
	H	2.21877700	0.13164500	1.41604700
	C	3.29019400	-0.04403600	-0.43118000
	H	3.57457000	1.01349100	-0.51331200
	H	4.14465300	-0.57809700	-0.00031700
	H	3.15481400	-0.41878400	-1.45424300
C4H9CHO	C	2.17944900	0.20894000	-0.00001600
	O	2.39295400	-0.95227700	-0.00005000
	H	3.02474700	0.95869000	-0.00000400
	C	0.82385400	0.82266800	0.00001400
	H	0.77836900	1.50642600	0.86657900
	H	0.77835200	1.50647300	-0.86651400
	C	-0.30850800	-0.15838300	-0.00000100
	H	-0.21142700	-0.82486800	-0.87166300
	H	-0.21141000	-0.82491500	0.87162200
	C	-1.66153300	0.49689200	0.00003000
	H	-1.74613100	1.16241700	-0.87560000
	H	-1.74611400	1.16237100	0.87569500
	C	-2.78969100	-0.49232300	0.00001500
	H	-3.77116200	-0.00471800	0.00003600
	H	-2.75014800	-1.14518600	-0.88192000
	H	-2.75013200	-1.14523100	0.88191700
C5	C	2.47014400	-0.95196100	0.65114800
	O	1.76120700	-1.22346600	-0.31821500
	O	1.67376900	-0.31357700	-1.27518600
	H	3.03916300	-0.01897600	0.66984200
	H	2.48516900	-1.70703000	1.43989700
	O	0.78682800	0.89958600	1.23198800
	C	0.64758600	1.48859600	0.20575500
	H	1.49127900	2.07926100	-0.24501200

	C	-0.63793800	1.61534600	-0.53348100
	H	-0.86418100	2.69605100	-0.53742600
	H	-0.43347100	1.37663200	-1.58906000
	C	-1.78053000	0.81279600	0.01964700
	H	-1.86643000	1.00219600	1.10209600
	H	-2.72168000	1.17897900	-0.42124500
	C	-1.66681900	-0.66861600	-0.22221400
	H	-0.76186000	-1.05188200	0.27067200
	H	-1.51126600	-0.85083300	-1.29809900
	C	-2.87085800	-1.42049400	0.26356800
	H	-3.78839400	-1.07970600	-0.23561900
	H	-2.78786600	-2.49915100	0.08652600
	H	-3.02440000	-1.27988100	1.34219900
TS5	C	-2.74685300	-0.65155400	-0.52178200
	O	-1.95324100	-1.22586600	0.23969600
	O	-1.57195400	-0.40534600	1.24721100
	H	-3.32499400	0.20352100	-0.16340000
	H	-2.99459700	-1.19237200	-1.43979800
	O	-1.31573600	0.69461300	-1.09620300
	C	-0.96901800	1.17008100	-0.03047000
	H	-1.65664100	1.83196900	0.54944300
	C	0.45589800	1.20792600	0.39281600
	H	0.84085700	2.19899800	0.08697700
	H	0.49322300	1.21322300	1.49159300
	C	1.29579400	0.10960200	-0.18751500
	H	0.85108700	-0.85897000	0.09252100
	H	1.24576200	0.14910500	-1.28671600
	C	2.72851200	0.16540100	0.26390300
	H	3.16034800	1.14467300	-0.00408100
	H	2.76669800	0.12520300	1.36526900
	C	3.56621000	-0.93651000	-0.31545100
	H	3.57664100	-0.89798800	-1.41298400
	H	4.60837300	-0.88986500	0.02121000
	H	3.17742700	-1.92438200	-0.03467600
P5	C	2.87471800	-0.08357100	-0.32896600
	O	2.07619000	0.98425600	-0.63532400
	O	1.30164400	1.00434500	0.54979000
	H	3.64689900	0.19232600	0.41901600
	H	3.34387100	-0.43052400	-1.26332300
	O	2.02194600	-1.03593900	0.17159200
	C	0.91886200	-0.32804000	0.61957500
	C	-0.29466700	-0.64695200	-0.19987600
	H	-0.08735400	-0.33945500	-1.23636100
	H	-0.40769900	-1.74155000	-0.22139100
	H	0.74243300	-0.51410300	1.69947400
	C	-1.53902800	0.00952000	0.32252600
	H	-1.38605400	1.10054700	0.37035600
	H	-1.71329700	-0.30538400	1.36703100
	C	-2.76297900	-0.29142900	-0.49715000
	H	-2.58752800	0.02551300	-1.53845400
	H	-2.90705000	-1.38358400	-0.54886300
	C	-4.00288200	0.36414400	0.03557100

	H	-4.88700800	0.13898300	-0.57172900
	H	-4.22144200	0.03703300	1.06096100
	H	-3.89816000	1.45686500	0.06472600
$C_5H_{11}CHO$	C	2.79255500	0.24359400	-0.00000200
	O	3.03703800	-0.91153700	-0.00001600
	H	3.61748900	1.01574600	0.00000600
	C	1.42098800	0.82066100	0.00000700
	H	1.35711700	1.50296800	0.86654000
	H	1.35711500	1.50298900	-0.86651000
	C	0.31554900	-0.19081800	-0.00000400
	H	0.43170700	-0.85398400	-0.87169200
	H	0.43171100	-0.85400500	0.87166800
	C	-1.05361200	0.42749700	0.00000700
	H	-1.16113700	1.09175300	-0.87613100
	H	-1.16113300	1.09173200	0.87616100
	C	-2.16918900	-0.58037200	-0.00000300
	H	-2.05935600	-1.24167900	0.87535200
	H	-2.05936000	-1.24165800	-0.87537500
	C	-3.53186900	0.04744200	0.00000700
	H	-4.33481800	-0.69854100	0.00000000
	H	-3.68108100	0.68446700	0.88217900
	H	-3.68108500	0.68448800	-0.88214800
C6	C	-3.19606200	-1.08114800	-0.60727700
	O	-2.31289000	-1.39392500	0.19110900
	O	-2.18620400	-0.63445000	1.26962100
	H	-3.87016400	-0.25133800	-0.38067500
	H	-3.24527600	-1.69706300	-1.50778200
	O	-1.86042800	1.00776800	-1.05924400
	C	-1.51335700	1.40631700	0.00961600
	H	-2.22334200	1.96200400	0.68085100
	C	-0.11876900	1.32579800	0.52067700
	H	0.27527000	2.35932000	0.48972200
	H	-0.16261000	1.07765900	1.59142100
	C	0.76561900	0.38469200	-0.23895000
	H	0.32929400	-0.62653500	-0.19116300
	H	0.75720600	0.65316000	-1.30697400
	C	2.17672900	0.35437700	0.27511100
	H	2.17508200	0.08996200	1.34726800
	H	2.60960300	1.36997300	0.23116900
	C	3.06891100	-0.59836200	-0.47090300
	H	3.06670400	-0.33408800	-1.54157600
	H	2.63563000	-1.61124100	-0.42337000
	C	4.47659900	-0.61929700	0.04813500
	H	5.11555400	-1.31813800	-0.50415100
	H	4.94489900	0.37189100	-0.02045200
	H	4.51031600	-0.91497300	1.10537000
TS6	C	-3.22949000	-0.77222300	-0.51752200
	O	-2.38602600	-1.31653500	0.21171300
	O	-2.04407500	-0.50665400	1.24174000
	H	-3.85814400	0.02864600	-0.12092500
	H	-3.45576300	-1.29738300	-1.45004800
	O	-1.90314100	0.68696700	-1.06574800

	C	-1.57304300	1.14994900	0.01069100
	H	-2.29579800	1.74184200	0.62267200
	C	-0.14757400	1.27346600	0.41514000
	H	0.16241600	2.29895900	0.13923600
	H	-0.09290200	1.24381000	1.51278500
	C	0.75684700	0.25674800	-0.21508500
	H	0.38280200	-0.74883800	0.03589700
	H	0.68676300	0.33168800	-1.31120400
	C	2.18791600	0.39535100	0.21991600
	H	2.55336400	1.41041900	-0.01888800
	H	2.24985700	0.32025100	1.32001600
	C	3.10583600	-0.62133000	-0.39980800
	H	3.04250600	-0.54502500	-1.49812600
	H	2.73882300	-1.63302500	-0.15997200
	C	4.53252400	-0.47629200	0.04174900
	H	5.19003700	-1.22413800	-0.41660000
	H	4.93519100	0.51221100	-0.21756400
	H	4.62868000	-0.58365800	1.13059500
P6	C	3.39235700	-0.07220400	-0.44693600
	O	2.57543300	0.99988700	-0.68150700
	O	1.87565400	0.99437100	0.54937200
	H	4.20934800	0.19026300	0.25697800
	H	3.80277000	-0.39925700	-1.41551200
	O	2.57324900	-1.03627200	0.08635100
	C	1.49900100	-0.33994200	0.61534000
	C	0.23783700	-0.64475000	-0.13462400
	H	0.38144000	-0.31697500	-1.17564000
	H	0.12412400	-1.73886800	-0.17057800
	H	1.38927500	-0.54827200	1.69999300
	C	-0.97254300	-0.00028500	0.47553400
	H	-0.81638400	1.08961900	0.53428000
	H	-1.08120500	-0.33543100	1.52250100
	C	-2.24327300	-0.28782200	-0.27271600
	H	-2.13700800	0.04944500	-1.31869900
	H	-2.39406800	-1.37997900	-0.33824200
	C	-3.46156600	0.34871800	0.33590700
	H	-3.56496700	0.00931900	1.38013000
	H	-3.30651500	1.43845100	0.40154800
	C	-4.72190200	0.05602000	-0.42381900
	H	-4.91847400	-1.02333700	-0.47542600
	H	-5.60219400	0.52414700	0.03148900
	H	-4.66029300	0.41857300	-1.45866600
CH_2FCHO	O	-1.79026700	0.08030800	-0.00000100
	C	-0.69671800	-0.35478400	0.00000100
	C	0.53640700	0.49759900	0.00000100
	H	0.52349400	1.15171400	-0.88819800
	H	0.52349300	1.15171400	0.88819800
	H	-0.47028200	-1.46075600	0.00000100
	F	1.63414400	-0.26022500	-0.00000100
C7	C	-2.19395700	0.22367300	0.49570600
	O	-1.84597000	-0.64783900	-0.30168800
	O	-0.68490100	-1.24099500	-0.06563900

	H	-3.12642500	0.73409100	0.24450000
	O	-0.18538500	1.53434300	-0.22867400
	C	0.62300000	0.70055000	-0.49388400
	C	1.67283200	0.25185400	0.47346800
	H	2.32736700	1.11487100	0.69522100
	H	1.19459000	-0.06101100	1.41497100
	H	0.73530600	0.25991800	-1.51910900
	F	2.39832700	-0.74314300	-0.03437000
	H	-1.59697700	0.41988500	1.39000200
TS7	C	1.44439000	0.93619100	-0.20332800
	O	1.79551500	-0.25151100	-0.27403300
	O	0.77712000	-1.04482400	-0.65638400
	H	2.17963600	1.60626400	0.25204400
	O	0.06086400	0.42164200	1.31808600
	C	-0.50512100	-0.52986800	0.82064600
	C	-1.66977300	-0.38313800	-0.10614900
	H	-1.68360900	-1.20375000	-0.83939500
	H	-2.59803100	-0.44489600	0.49280500
	H	-0.42913900	-1.54697700	1.27413100
	F	-1.63367800	0.79618400	-0.73608400
	H	0.54927100	1.28213800	-0.72320300
P7	C	-1.84706300	0.43093900	0.18906000
	O	-1.63348300	-0.87738800	-0.15740000
	O	-0.29150100	-1.00295600	0.26429900
	H	-2.71695200	0.78457000	-0.38859600
	O	-0.69482000	1.09615700	-0.17431100
	C	0.23869500	0.09911600	-0.36734400
	C	1.53237000	0.48735100	0.28308300
	H	1.77146500	1.51899600	-0.01816000
	H	1.41702500	0.45824400	1.37857400
	H	0.38152100	-0.10336300	-1.45129400
	F	2.50983200	-0.33732300	-0.09854100
	H	-2.02712400	0.54652700	1.27686000
CHF_2CHO	O	-1.96861300	-0.00000400	-0.20462000
	C	-0.94530900	-0.00000900	0.36994900
	C	0.41435800	-0.00000100	-0.32568900
	H	0.31325300	-0.00000100	-1.42741900
	H	-0.85708400	-0.00002000	1.49342600
	F	1.08212300	1.06248200	0.07252300
	F	1.08214800	-1.06247000	0.07252000
C8	C	-2.05220300	0.25125100	0.80215400
	O	-2.18255500	-0.28815000	-0.29839800
	O	-1.16986500	-1.06552000	-0.67752800
	H	-2.85446200	0.94359200	1.07049500
	O	-0.20307100	1.43685100	-0.15057700
	C	0.36846600	0.57449800	-0.73932000
	C	1.31770200	-0.40001500	-0.05089400
	H	1.20088800	-1.43276700	-0.42655700
	H	0.38506200	0.50388700	-1.85469100
	F	2.55539700	0.01175600	-0.28168600
	H	-1.21189100	-0.01008200	1.45045400
	F	1.12466200	-0.37003200	1.24842900

TS8	C	1.92536200	-0.81158000	-0.24436700
	O	2.13050500	0.28417900	0.29421000
	O	1.08221500	0.70405100	1.02082400
	H	2.69551800	-1.12408400	-0.95561600
	O	0.30696100	0.10125300	-1.37757300
	C	-0.26361200	0.72225400	-0.51512300
	C	-1.30370800	0.07938000	0.39042800
	H	-1.27997100	0.49542500	1.41478100
	H	-0.30392000	1.83615100	-0.51573500
	F	-2.49900200	0.28850600	-0.13700500
	H	1.10921400	-1.45297700	0.09273300
	F	-1.11505900	-1.22302900	0.43461800
P8	C	1.98785000	-0.58169700	0.30551100
	O	2.03601000	0.68433200	-0.21090200
	O	0.71842300	1.09416000	0.09060600
	H	2.82110600	-1.15219000	-0.13424500
	O	0.77212800	-1.08666000	-0.10511600
	C	0.01754500	0.02199500	-0.40635400
	C	-1.31220400	-0.03498600	0.31815500
	H	-1.16075200	-0.12217300	1.41247400
	H	-0.14960500	0.09706300	-1.50283600
	F	-2.00599700	1.04707400	0.04590400
	H	2.05460500	-0.57613500	1.41218300
	F	-1.98700200	-1.07075000	-0.12236500
CF_3CHO	O	2.01691100	0.13322100	0.00000000
	C	1.06847400	-0.55203800	0.00000000
	C	-0.36641700	0.00480600	0.00000000
	H	1.09375200	-1.67536500	0.00000000
	F	-0.99836400	-0.42921200	1.05263200
	F	-0.38564500	1.29098400	-0.00000300
	F	-0.99836600	-0.42921700	-1.05262900
C8	C	2.24579400	-0.39590400	0.69104500
	O	2.26681000	0.46177500	-0.19533200
	O	1.13329200	1.15750300	-0.32130600
	H	1.42016300	-0.43410800	1.40501000
	H	3.13534200	-1.03026500	0.73650500
	O	0.56747800	-1.42973700	-0.54361300
	C	-0.09518000	-0.48630400	-0.85771400
	C	-1.19983900	0.04791300	0.05936800
	H	-0.15149100	-0.08213800	-1.89481900
	F	-2.28797600	-0.64754500	-0.14749900
	F	-0.88528800	-0.08140800	1.31369900
	F	-1.47665900	1.28850300	-0.17963200
TS8	C	2.23280600	-0.39850500	0.68885500
	O	2.26023800	0.46705400	-0.19037400
	O	1.12166100	1.15699700	-0.31649100
	H	1.40874500	-0.43560000	1.40439000
	H	3.12043400	-1.03582500	0.73289100
	O	0.58218300	-1.41809400	-0.54766500
	C	-0.08289900	-0.47228300	-0.85666100
	C	-1.19642000	0.04528800	0.05837700
	H	-0.14505200	-0.06954700	-1.89371800

	F	-2.27809200	-0.65698200	-0.15778900
	F	-0.88637200	-0.09018300	1.31356800
	F	-1.48194800	1.28564300	-0.17253000
P8	C	2.03049700	-0.61590100	0.32861000
	O	2.20270900	0.67132400	-0.09771400
	O	0.86624300	1.11117200	0.00626100
	H	1.86201900	-0.66467700	1.42231100
	H	2.91908700	-1.19327300	0.03338000
	O	0.91989800	-1.05678300	-0.36159700
	C	0.20160700	0.07956100	-0.61771800
	C	-1.18219500	-0.00587300	0.02083900
	H	0.09107400	0.23062400	-1.71215900
	F	-1.86562800	-0.95358800	-0.54322900
	F	-1.09489000	-0.26029800	1.28763400
	F	-1.82641900	1.11109700	-0.13435200

Table S32. Absolute energies in Hartrees

Species	Methods	Total energies (a.u.)
CH_2OO	CCSD(T)-F12a/cc-pVTZ-F12	-189.405683
	CCSD(T)-F12a/cc-pVDZ-F12	-189.381569
	DF-CCSD(T)-F12b/jun-cc-pVDZ	-189.276824
	DF-CCSD(T)-F12b/cc-pVDZ	-189.261787
	DF-CCSD(T)-F12b/VDZ(NP)	-189.159752
	DF-CCSD(T)-F12b/VDZ(D)	-189.251674
	M11-L/MG3S	-189.582948
HCHO	CCSD(T)-F12a/cc-pVTZ-F12	-114.387945
	CCSD(T)-F12a/cc-pVDZ-F12	-114.373877
	DF-CCSD(T)-F12b/jun-cc-pVDZ	-114.313291
	DF-CCSD(T)-F12b/cc-pVDZ	-114.304602
	DF-CCSD(T)-F12b/VDZ(NP)	-114.232172
	DF-CCSD(T)-F12b/VDZ(D)	-114.294812
	M11-L/MG3S	-114.509429
C1	CCSD(T)-F12a/cc-pVTZ-F12	-303.807856
	M11-L/MG3S	-341.260635
TS1	CCSD(T)-F12a/cc-pVTZ-F12	-303.807354
	CCSD(T)-F12a/cc-pVDZ-F12	-303.768782
	DF-CCSD(T)-F12b/jun-cc-pVDZ	-303.540353
	DF-CCSD(T)-F12b/cc-pVDZ	-303.581219
	DF-CCSD(T)-F12b/VDZ(NP)	-303.409076
	DF-CCSD(T)-F12b/VDZ(D)	-303.561584
	M11-L/MG3S	-304.104857
P1	CCSD(T)-F12a/cc-pVTZ-F12	-303.885292
	M11-L/MG3S	-304.181539
CH_3CHO	CCSD(T)-F12a/cc-pVDZ-F12	-153.640268
	DF-CCSD(T)-F12b/jun-cc-pVDZ	-153.557475
	DF-CCSD(T)-F12b/cc-pVDZ	-153.548482
	DF-CCSD(T)-F12b/VDZ(NP)	-153.446309
	DF-CCSD(T)-F12b/VDZ(D)	-153.529317
	M11-L/MG3S	-153.844297
C2	DF-CCSD(T)-F12b/jun-cc-pVDZ	-342.845685
	M11-L/MG3S	-343.43688
TS2a	CCSD(T)-F12a/cc-pVDZ-F12	-343.031482
	DF-CCSD(T)-F12b/jun-cc-pVDZ	-342.844805
	DF-CCSD(T)-F12b/cc-pVDZ	-342.821732
	DF-CCSD(T)-F12b/VDZ(NP)	-342.619902
	DF-CCSD(T)-F12b/VDZ(D)	-342.792314
	M11-L/MG3S	-343.435864
C2a	DF-CCSD(T)-F12b/jun-cc-pVDZ	-342.848809
	M11-L/MG3S	-343.440041
TS2c	CCSD(T)-F12a/cc-pVDZ-F12	-343.033960
	DF-CCSD(T)-F12b/jun-cc-pVDZ	-342.846147
	DF-CCSD(T)-F12b/cc-pVDZ	-342.824491
	DF-CCSD(T)-F12b/VDZ(NP)	-342.623317
	DF-CCSD(T)-F12b/VDZ(D)	-342.705493
	M11-L/MG3S	-343.437212
P2c	DF-CCSD(T)-F12b/jun-cc-pVDZ	-342.921406

	M11-L/MG3S	-343.512027
C_2H_5CHO	DF-CCSD(T)-F12b/jun-cc-pVDZ	-192.789725
	DF-CCSD(T)-F12b/cc-pVDZ	-192.781196
	DF-CCSD(T)-F12b/VDZ(D)	-192.753125
	M11-L/MG3S	-193.163907
C3	M11-L/MG3S	-382.759889
TS3	DF-CCSD(T)-F12b/jun-cc-pVDZ	-382.078713
	DF-CCSD(T)-F12b/cc-pVDZ	-382.057983
	DF-CCSD(T)-F12b/VDZ(D)	-382.020079
	M11-L/MG3S	-382.757103
P3	M11-L/MG3S	-382.829934
C_3H_7CHO	DF-CCSD(T)-F12b/jun-cc-pVDZ	-232.021020
	DF-CCSD(T)-F12b/cc-pVDZ	-232.012036
	DF-CCSD(T)-F12b/VDZ(D)	-231.975024
	M11-L/MG3S	-232.482428
C4	M11-L/MG3S	-422.077763
TS4	DF-CCSD(T)-F12b/jun-cc-pVDZ	-421.310265
	DF-CCSD(T)-F12b/cc-pVDZ	-421.288959
	DF-CCSD(T)-F12b/VDZ(D)	-421.242111
	M11-L/MG3S	-422.075669
P4	M11-L/MG3S	-422.148588
C_4H_9CHO	DF-CCSD(T)-F12b/jun-cc-pVDZ	-271.252756
	DF-CCSD(T)-F12b/cc-pVDZ	-271.243162
	DF-CCSD(T)-F12b/VDZ(D)	-271.197232
	M11-L/MG3S	-271.801365
C5	M11-L/MG3S	-461.396844
TS5	DF-CCSD(T)-F12b/jun-cc-pVDZ	-460.542095
	DF-CCSD(T)-F12b/cc-pVDZ	-460.520167
	DF-CCSD(T)-F12b/VDZ(D)	-460.464410
	M11-L/MG3S	-461.39462
P5	M11-L/MG3S	-461.467575
$C_5H_{11}CHO$	DF-CCSD(T)-F12b/VDZ(D)	-310.419413
	M11-L/MG3S	-311.120255
C6	M11-L/MG3S	-500.716305
TS6	DF-CCSD(T)-F12b/VDZ(D)	-499.686473
	M11-L/MG3S	-500.786442
P6	M11-L/MG3S	-500.713502
CH_2FCHO	DF-CCSD(T)-F12b/jun-cc-pVDZ	-252.662927
	M11-L/MG3S	-253.067811
C7	M11-L/MG3S	-442.664006
TS7	DF-CCSD(T)-F12b/jun-cc-pVDZ	-441.955104
	M11-L/MG3S	-442.664155
P7	M11-L/MG3S	-442.735262
CHF_2CHO	DF-CCSD(T)-F12b/jun-cc-pVDZ	-351.781899
	M11-L/MG3S	-352.309047
C8	M11-L/MG3S	-541.909455
TS8	DF-CCSD(T)-F12b/jun-cc-pVDZ	-541.076681
	M11-L/MG3S	-541.908896
P8	M11-L/MG3S	-541.981018
CF_3CHO	M11-L/MG3S	-451.567135

C9	M11-L/MG3S	-641.168621
TS9	M11-L/MG3S	-641.168619
P9	M11-L/MG3S	-641.239908

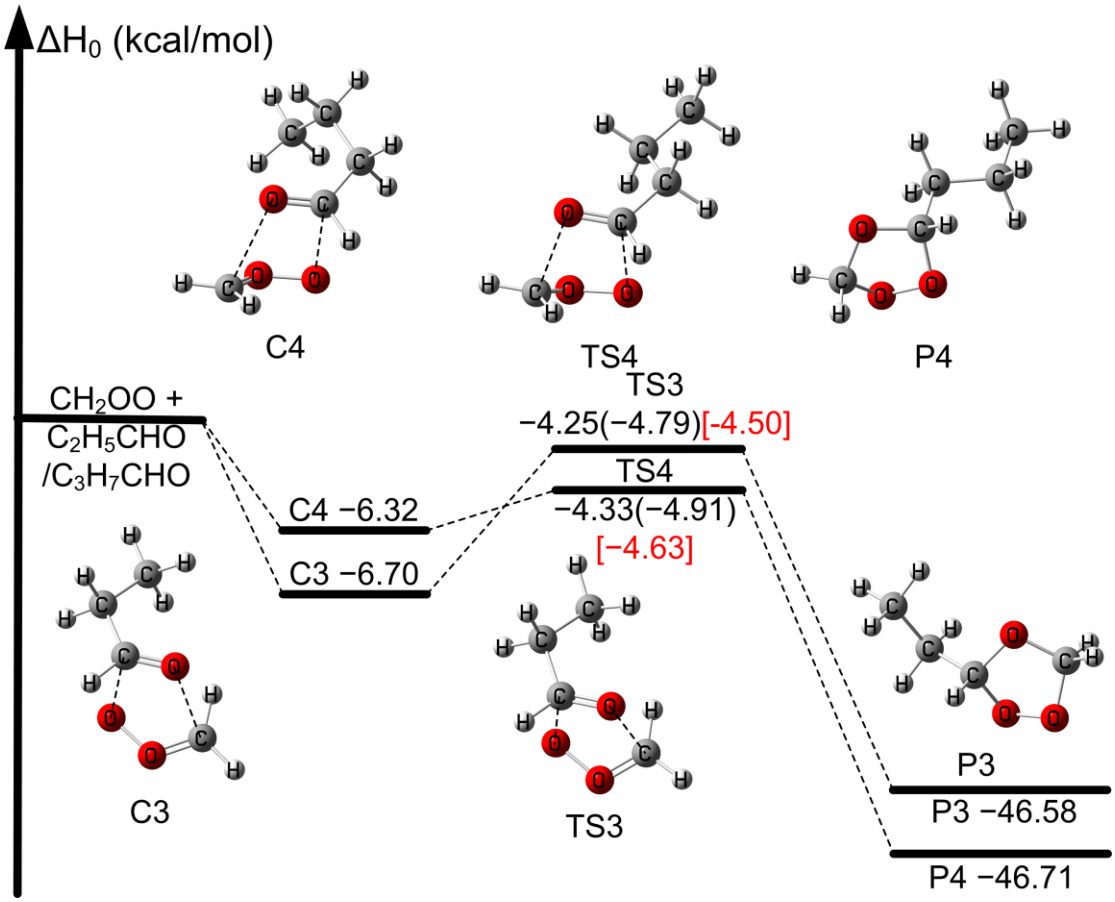


Figure S1. The relative enthalpies at 0 K for the reaction of CH_2OO + RCHO (R= C_2H_5/C_3H_7). Values are given for all species as calculated by M11-L/MG3S, and in parentheses and bracket, values are given for the transition state TS path as calculated by W3X-L and BE1.

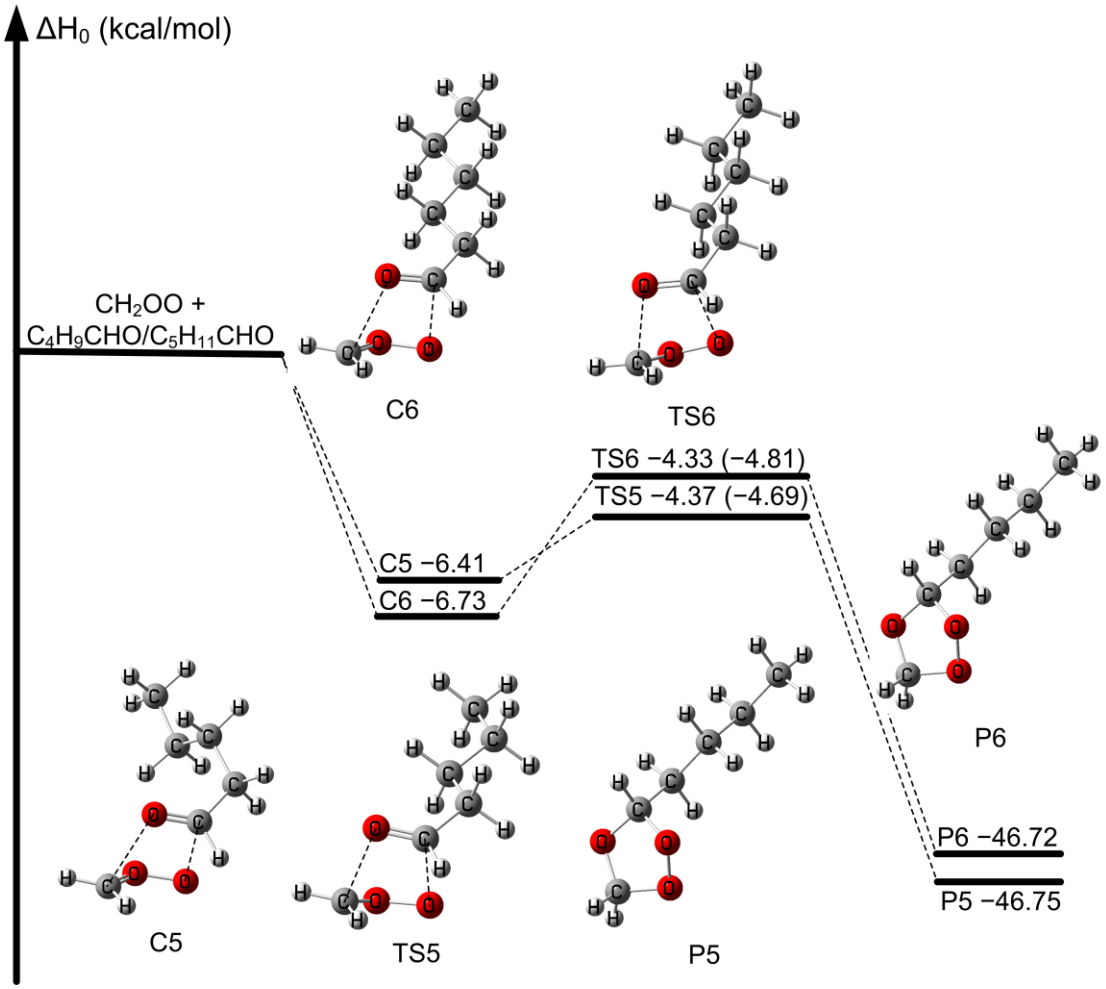


Figure S2. The relative enthalpies at 0 K for the reaction of CH_2OO + RCHO (R = C_4H_9/C_5H_{11}). Values are given for all species as calculated by M11-L/MG3S, and in parentheses, values are given for the transition state TS path as calculated by BE1.

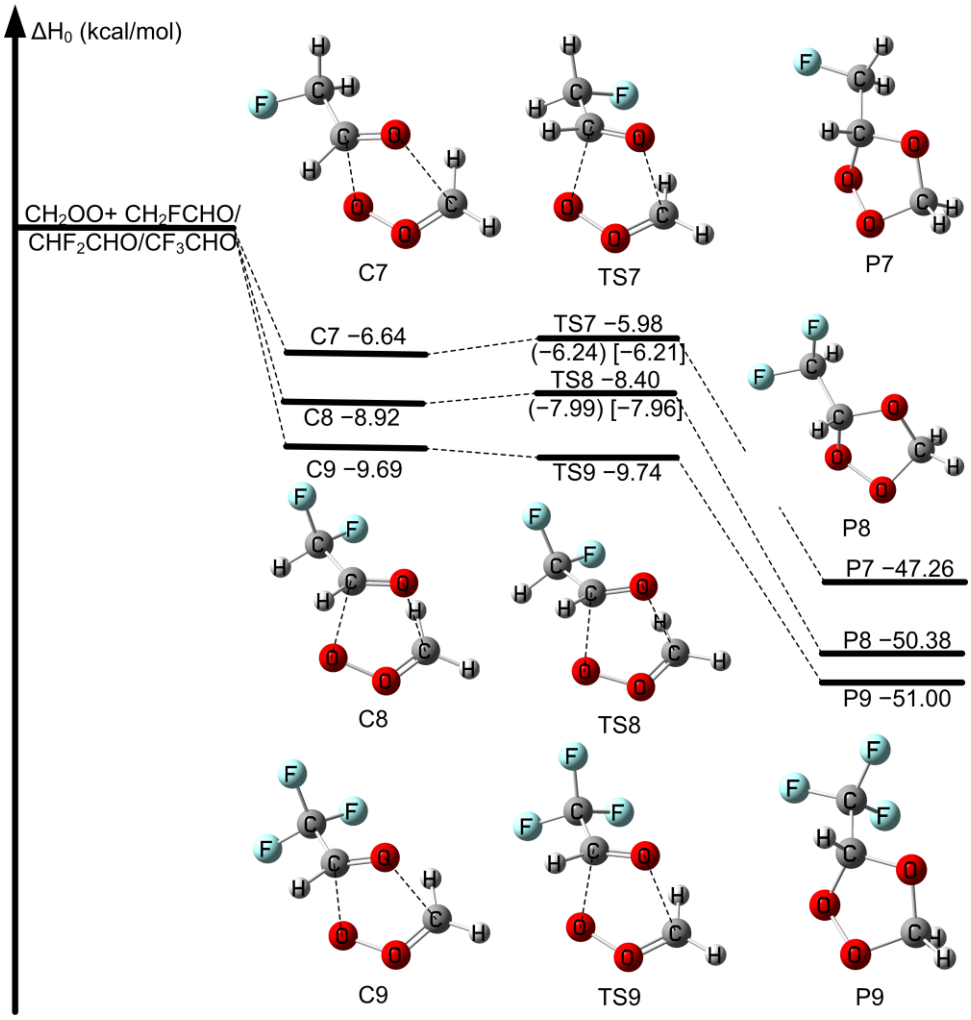


Figure S3. The relative enthalpies at 0 K for the reaction of CH_2OO + $CH_2FCHO/CHF_2CHO/CF_3CHO$. in parentheses and bracket, values are given for the transition states as calculated by BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ and BE2//DF-CCSD(T)-F12b/jun-cc-pVDZ.

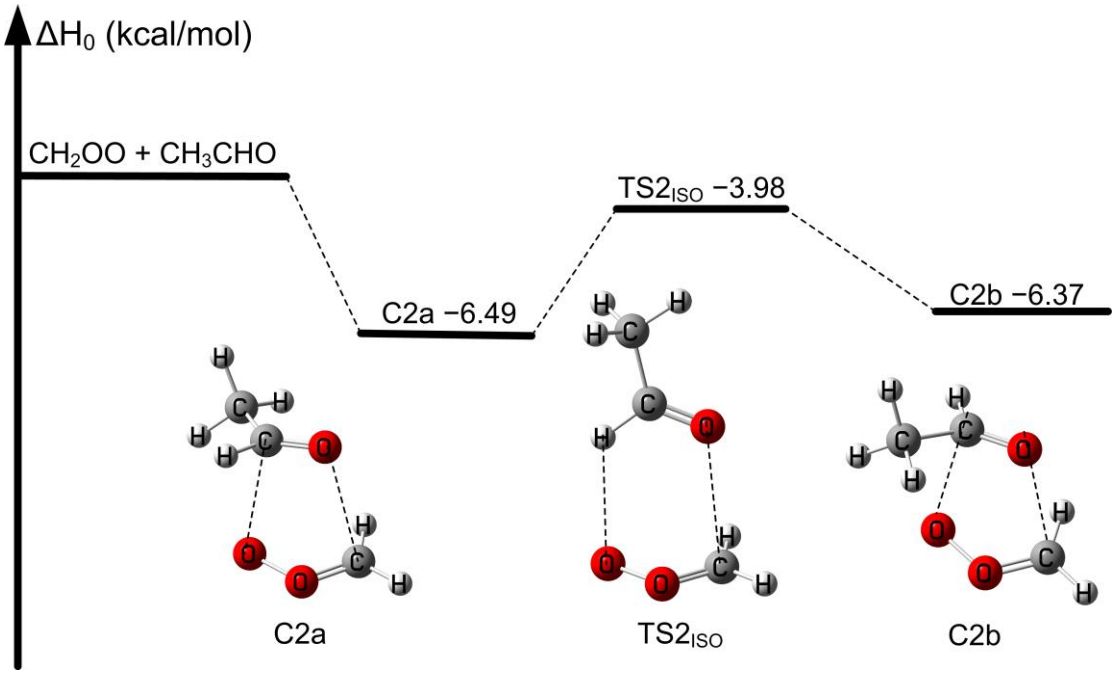


Figure S4. Enthalpy profile at 0 K for the conversion of C2b to C2d as calculated by M11-L/MG3S.

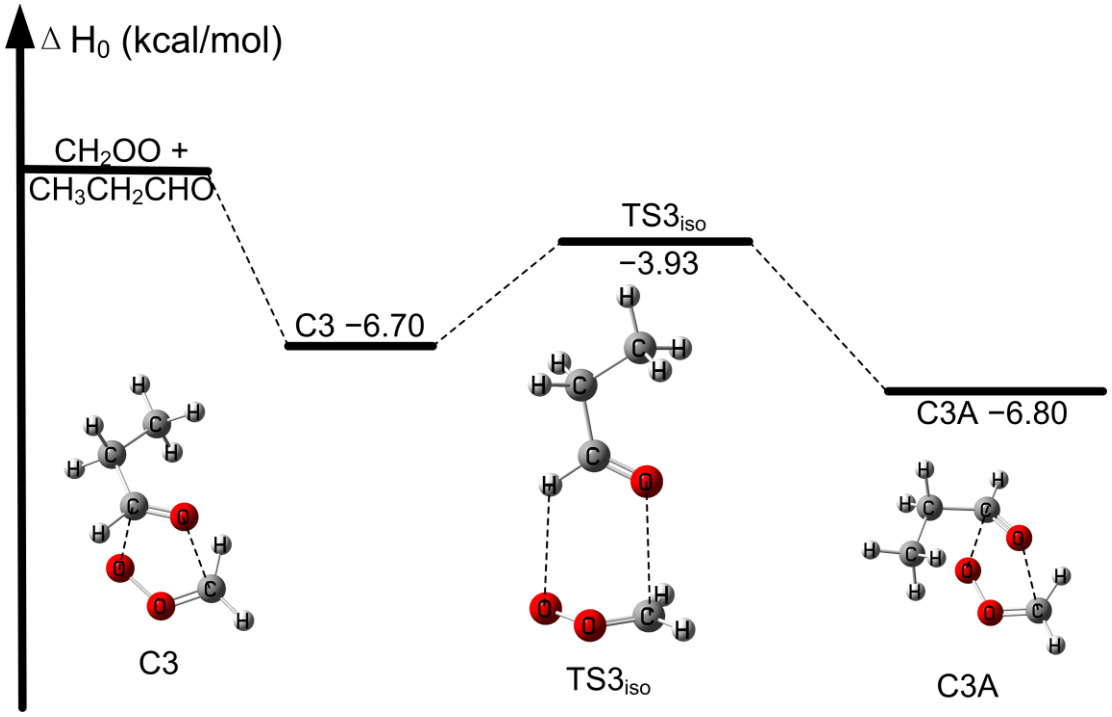


Figure S5. Enthalpy profile at 0 K for the conversion of C3 to C3A as calculated by M11-L/MG3S.

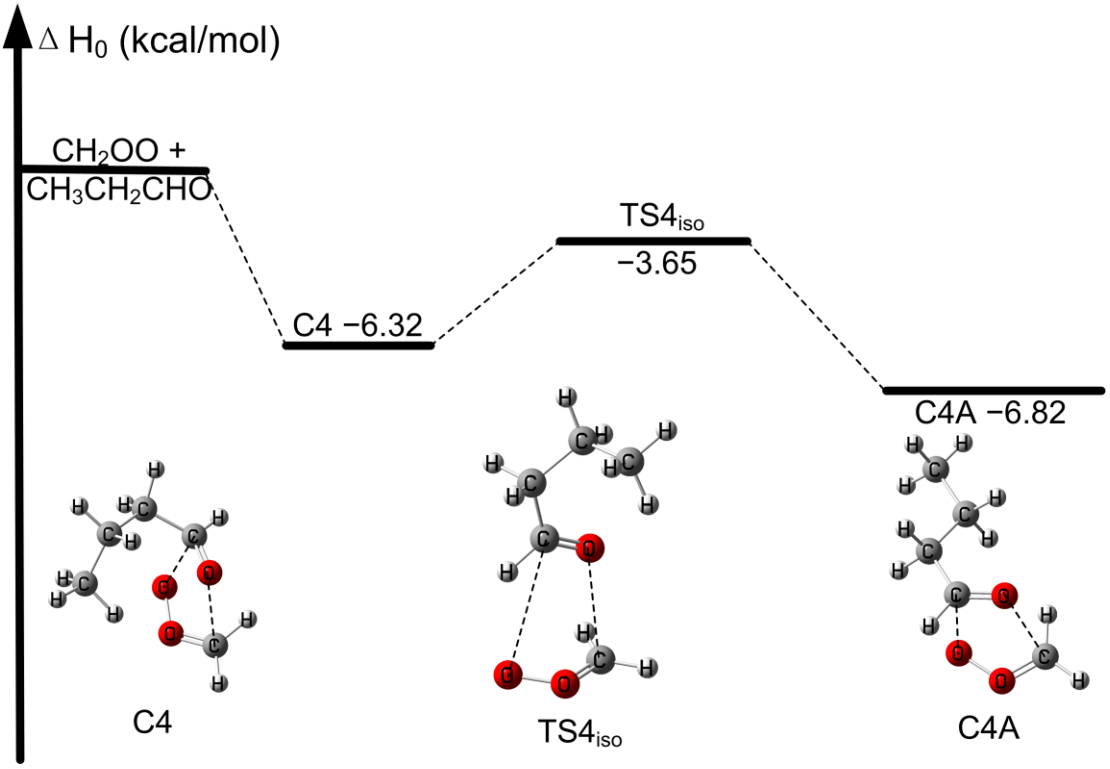


Figure S6. Enthalpy profile at 0 K for the conversion of C4 to C4A as calculated by M11-L/MG3S.

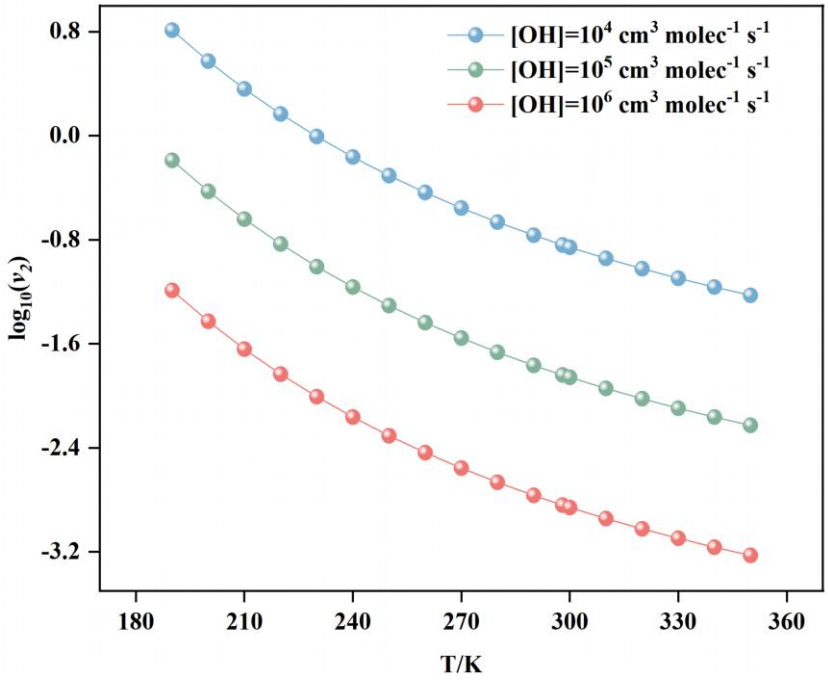


Figure S7. The rate ratio v_2 between the reaction of CH_2OO + CH_3CHO and OH + CH_3CHO at [CH_2OO] = 10^4 molecules cm^{-3} with different concentrations of OH in the temperature range of 190−350 K.

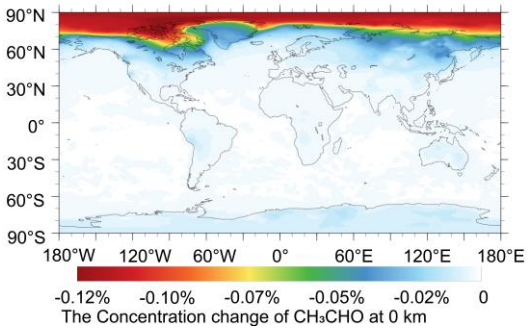


Figure S8. Changes in global CH_3CHO concentrations due to reaction R2.

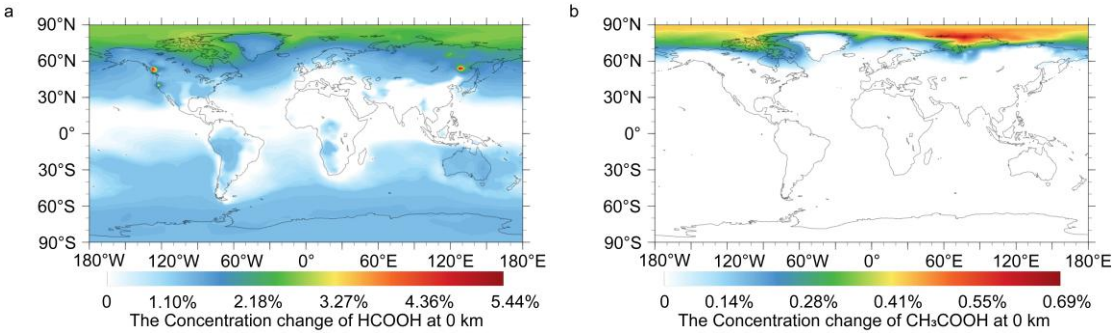


Figure S9. Changes in global HCOOH and CH_3COOH concentrations due to reactions R1 and R2, (a) the concentration change of HCOOH due to reaction R1, (b) the concentration change of CH_3COOH due to reaction R2.

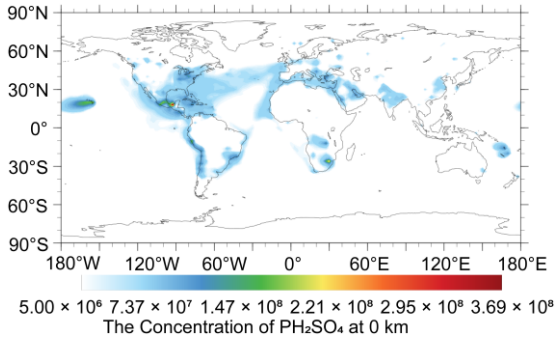


Figure S10. Global PH_2SO_4 concentrations in "base" version.

Reference

Berndt, T., Kaethner, R., Voigtländer, J., Stratmann, F., Pfeifle, M., Reichle, P., Sipilä, M., Kulmala, M., and Olzmann, M.: Kinetics of the unimolecular reaction of CH_2OO and the bimolecular reactions with the water monomer, acetaldehyde and acetone under atmospheric conditions, PCCP, 17, 19862-19873, 10.1039/C5CP02224J, 2015.

Kuwata, K. T., Hermes, M. R., Carlson, M. J., and Zogg, C. K.: Computational Studies of the Isomerization and Hydration Reactions of Acetaldehyde Oxide and Methyl Vinyl Carbonyl Oxide, The Journal of Physical Chemistry A, 114, 9192-9204, 10.1021/jp105358v, 2010.

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, 10.1021/jacs.6b08655, 2016.

Long, B., Bao, J. L., and Truhlar, D. G.: Kinetics of the Strongly Correlated CH3O + O2 Reaction: The Importance of Quadruple Excitations in Atmospheric and Combustion Chemistry, J. Am. Chem. Soc., 141, 611-617, 10.1021/jacs.8b11766, 2019.

Long, B., Xia, Y., and Truhlar, D. G.: Quantitative Kinetics of HO2 Reactions with Aldehydes in the Atmosphere: High-Order Dynamic Correlation, Anharmonicity, and Falloff Effects Are All Important, J. Am. Chem. Soc., 144, 19910-19920, 10.1021/jacs.2c07994, 2022.

Long, B., Xia, Y., Zhang, Y.-Q., and Truhlar, D. G.: Kinetics of Sulfur Trioxide Reaction with Water Vapor to Form Atmospheric Sulfuric Acid, J. Am. Chem. Soc., 145, 19866-19876, 10.1021/jacs.3c06032, 2023.

Long, B., Wang, Y., Xia, Y., He, X., Bao, J. L., and Truhlar, D. G.: Atmospheric Kinetics: Bimolecular Reactions of Carbonyl Oxide by a Triple-Level Strategy, J. Am. Chem. Soc., 143, 8402-8413, 10.1021/jacs.1c02029, 2021.

Sun, Y., Long, B., and Truhlar, D. G.: Unimolecular Reactions of E-Glycolaldehyde Oxide and Its Reactions with One and Two Water Molecules, Research, 6, 0143, 10.34133/research.0143, 2024.

Xia, Y., Zhang, W., Tang, X., and Long, B.: Quantitative Kinetics of the Hydrogen Shift Reaction of Methylthiomethyl Peroxy Radical (CH3SCH2OO) in the Atmosphere, The Journal of Physical Chemistry A, 129, 2275-2285, 10.1021/acs.jpca.4c06818, 2025.

Zheng, J. and Truhlar, D. G.: Multi-path variational transition state theory for chemical reaction rates of complex polyatomic species: ethanol + OH reactions, Faraday Discuss., 157, 59-88, 10.1039/C2FD20012K, 2012.

Zheng, J., Mielke, S. L., Clarkson, K. L., and Truhlar, D. G.: MSTor: A program for calculating partition functions, free energies, enthalpies, entropies, and heat capacities of complex molecules including torsional anharmonicity, Comput. Phys. Commun., 183, 1803-1812, https://doi.org/10.1016/j.cpc.2012.03.007, 2012.