SUPPLEMENTARY MATERIAL

MAY 14, 2022

Temperature-dependent kinetics for the reaction between CH_2OO and acetone in the atmosphere

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General notation for electronic structure methods

L/B	This indicates that the electronic structure method L with basis set B is employed to do geometrical optimizations and frequency calculations.
DF-	When L is preceded by DF-, it means that density fitting of the two-electron integrals was employed.
CM//L/B	This indicates that single energy calculations are done by composite method (CM) based on the L/B optimized geometries.

Notation used for single-level electronic structure methods

CCSD(T)-F12b	same as CSD(T)-F12a except uses the F12b scheme instead of F12a for the explicit correlation.

Notation used for composite methods at the CCSD(T) level

W2X	an efficient method of extrapolation to the CCSD(T)/CBS(full) level.

Notation used for composite methods that go beyond CCSD(T)

W3X-L	a combination of nonrelativistic CCSD(T)/CBS(FC), scalar relativistic effects, and post-CCSD(T) and core−valence correlation contributions with the goal of approximating the CCSDT(Q)/CBS(full) energy.

Nomenclature used for transition states

transition structure	a first-order saddle pint connecting reactants to products (optimized by electronic structure calculations)
conventional transition state	a dividing surface (between reactants and products) passing through the saddle point and normal to the imaginary-frequency normal mode
variational transition state	a dividing surface optimized to minimize the ensemble averaged flux from reactants to products

Geometries used in composite methods

Method	*Geometries*
W2X	DF-CCSD(T)-F12b/jun-cc-pVDZ
W3X-L	DF-CCSD(T)-F12b/jun-cc-pVDZ

Dual-level method for rate constant calculations at tight transition states

The dual-level method for the rate constants is as follows:

L denotes level-L, which defines an implicit potential energy surface by direct dynamics;

HL denotes higher level.

The rate constant is calculated by combining HL rate constants calculated with conventional transition state theory (TST) and L direct dynamics rate constants calculated with canonical variational transition state theory with small-curvature tunneling (CVT/SCT):

$$k = \frac{k_{TST}^{HL}}{k_{TST}^{L}} k_{CVT/SCT}^{L} = k_{TST}^{HL} \frac{k_{SCT}^{L} k_{CVT}^{L}}{k_{TST}^{L}}$$

where

k_{TST}^{HL} is the TST rate constant calculated with HL;

k_{TST}^{L} is the TST rate constant calculated with L;

$k_{CVT/SCT}^{L}$ is the CVT/SCT rate constant calculated with L;

k_{SCT}^{L} is the SCT tunneling transmission coefficient calculated with L;

$k_{CVT/SCT}^{L}$ is the CVT rate constant calculated with L.

The levels used in the present work are given as follows:

High level (HL): W3X-L//DF-CCSD(T)-F12*b*/jun-cc-pVDZ

Lower level (L): M11-L/MG3S

Table S1. Scale factors for calculating vibrational frequencies different theoretical methods.

Methods	Scale Factor
DF-CCSD(T)-F12b/jun-cc-pVDZ	0.981
M11-L/MG3S	0.985
M06CR/MG3S	0.980
MN15-L/MG3S	0.977
M06-2X/MG3S	0.970
B3LYP/MG3S	0.983

Table S2. Rate constants (cm^3 $molecule^{-1}$ s^{-1}) for the CH_2OO + $CH_3C(O)CH_3$ reaction at the different temperatures and pressures[a]

P (bar)	T = 190 K	T = 200 K	T = 210 K	T = 220 K
0.00533	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.00666	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.00679	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0132	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0133	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.02	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0268	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0316	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0333	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.04	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0401	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0533	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.0666	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.08	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.1	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.107	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.133	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.134	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.178	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.316	1.33E-11	7.36E-12	4.33E-12	2.69E-12
0.562	1.33E-11	7.36E-12	4.33E-12	2.69E-12
1	1.33E-11	7.36E-12	4.33E-12	2.69E-12
1.01	1.33E-11	7.36E-12	4.33E-12	2.69E-12
1.78	1.33E-11	7.36E-12	4.33E-12	2.69E-12
2	1.33E-11	7.36E-12	4.33E-12	2.69E-12
3.16	1.33E-11	7.36E-12	4.33E-12	2.69E-12
5	1.33E-11	7.36E-12	4.33E-12	2.69E-12
5.62	1.33E-11	7.36E-12	4.33E-12	2.69E-12
10	1.33E-11	7.36E-12	4.33E-12	2.69E-12
31.6	1.33E-11	7.36E-12	4.33E-12	2.69E-12
50	1.33E-11	7.36E-12	4.33E-12	2.69E-12
100	1.33E-11	7.36E-12	4.33E-12	2.69E-12
1000	1.33E-11	7.36E-12	4.33E-12	2.69E-12
P (bar)	T = 230 K	T = 240 K	T = 250 K	T = 252 K
0.00533	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.00666	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.00679	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0132	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0133	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.02	1.75E-12	1.18E-12	8.28E-13	7.75E-13

0.0268	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0316	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0333	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.04	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0401	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0533	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.0666	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.08	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.1	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.107	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.133	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.134	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.178	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.316	1.75E-12	1.18E-12	8.28E-13	7.75E-13
0.562	1.75E-12	1.18E-12	8.28E-13	7.75E-13
1	1.75E-12	1.18E-12	8.28E-13	7.75E-13
1.01	1.75E-12	1.18E-12	8.28E-13	7.75E-13
1.78	1.75E-12	1.18E-12	8.28E-13	7.75E-13
2	1.75E-12	1.18E-12	8.28E-13	7.75E-13
3.16	1.75E-12	1.18E-12	8.28E-13	7.75E-13
5	1.75E-12	1.18E-12	8.28E-13	7.75E-13
5.62	1.75E-12	1.18E-12	8.28E-13	7.75E-13
10	1.75E-12	1.18E-12	8.28E-13	7.75E-13
31.6	1.75E-12	1.18E-12	8.28E-13	7.75E-13
50	1.75E-12	1.18E-12	8.28E-13	7.75E-13
100	1.75E-12	1.18E-12	8.28E-13	7.75E-13
1000	1.75E-12	1.18E-12	8.28E-13	7.75E-13
P (bar)	T = 254 K	T = 256 K	T = 258 K	T = 260 K
0.00533	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.00666	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.00679	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0132	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0133	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.02	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0268	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0316	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0333	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.04	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0401	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0533	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.0666	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.08	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.1	7.25E-13	6.79E-13	6.37E-13	5.99E-13

0.107	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.133	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.134	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.178	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.316	7.25E-13	6.79E-13	6.37E-13	5.99E-13
0.562	7.25E-13	6.79E-13	6.37E-13	5.99E-13
1	7.25E-13	6.79E-13	6.37E-13	5.99E-13
1.01	7.25E-13	6.79E-13	6.37E-13	5.99E-13
1.78	7.25E-13	6.79E-13	6.37E-13	5.99E-13
2	7.25E-13	6.79E-13	6.37E-13	5.99E-13
3.16	7.25E-13	6.79E-13	6.37E-13	5.99E-13
5	7.25E-13	6.79E-13	6.37E-13	5.99E-13
5.62	7.25E-13	6.79E-13	6.37E-13	5.99E-13
10	7.25E-13	6.79E-13	6.37E-13	5.99E-13
31.6	7.25E-13	6.79E-13	6.37E-13	5.99E-13
50	7.25E-13	6.79E-13	6.37E-13	5.99E-13
100	7.25E-13	6.79E-13	6.37E-13	5.99E-13
1000	7.25E-13	6.79E-13	6.37E-13	5.99E-13
P (bar)	T = 263 K	T = 270 K	T = 273 K	T = 280 K
0.00533	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.00666	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.00679	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0132	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0133	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.02	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0268	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0316	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0333	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.04	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0401	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0533	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.0666	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.08	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.1	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.107	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.133	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.134	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.178	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.316	5.46E-13	4.45E-13	4.09E-13	3.38E-13
0.562	5.46E-13	4.45E-13	4.09E-13	3.38E-13
1	5.46E-13	4.45E-13	4.09E-13	3.38E-13
1.01	5.46E-13	4.45E-13	4.09E-13	3.38E-13
1.78	5.46E-13	4.45E-13	4.09E-13	3.38E-13

2	5.46E-13	4.45E-13	4.09E-13	3.38E-13
3.16	5.46E-13	4.45E-13	4.09E-13	3.38E-13
5	5.46E-13	4.45E-13	4.09E-13	3.38E-13
5.62	5.46E-13	4.45E-13	4.09E-13	3.38E-13
10	5.46E-13	4.45E-13	4.09E-13	3.38E-13
31.6	5.46E-13	4.45E-13	4.09E-13	3.38E-13
50	5.46E-13	4.45E-13	4.09E-13	3.38E-13
100	5.46E-13	4.45E-13	4.09E-13	3.38E-13
1000	5.46E-13	4.45E-13	4.09E-13	3.38E-13
P (bar)	T = 283 K	T = 290 K	T = 293 K	T = 294 K
0.00533	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.00666	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.00679	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0132	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0133	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.02	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0268	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0316	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0333	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.04	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0401	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0533	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.0666	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.08	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.1	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.107	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.133	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.134	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.178	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.316	3.13E-13	2.63E-13	2.45E-13	2.39E-13
0.562	3.13E-13	2.63E-13	2.45E-13	2.39E-13
1	3.13E-13	2.63E-13	2.45E-13	2.39E-13
1.01	3.13E-13	2.63E-13	2.45E-13	2.39E-13
1.78	3.13E-13	2.63E-13	2.45E-13	2.39E-13
2	3.13E-13	2.63E-13	2.45E-13	2.39E-13
3.16	3.13E-13	2.63E-13	2.45E-13	2.39E-13
5	3.13E-13	2.63E-13	2.45E-13	2.39E-13
5.62	3.13E-13	2.63E-13	2.45E-13	2.39E-13
10	3.13E-13	2.63E-13	2.45E-13	2.39E-13
31.6	3.13E-13	2.63E-13	2.45E-13	2.39E-13
50	3.13E-13	2.63E-13	2.45E-13	2.39E-13
100	3.13E-13	2.63E-13	2.45E-13	2.39E-13
1000	3.13E-13	2.63E-13	2.45E-13	2.39E-13

P (bar)	T = 297 K	T = 298 K	T = 300 K	T = 302 K
0.00533	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.00666	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.00679	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0132	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0133	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.02	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0268	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0316	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0333	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.04	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0401	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0533	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.0666	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.08	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.1	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.107	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.133	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.134	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.178	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.316	2.23E-13	2.18E-13	2.09E-13	2.00E-13
0.562	2.23E-13	2.18E-13	2.09E-13	2.00E-13
1	2.23E-13	2.18E-13	2.09E-13	2.00E-13
1.01	2.23E-13	2.18E-13	2.09E-13	2.00E-13
1.78	2.23E-13	2.18E-13	2.09E-13	2.00E-13
2	2.23E-13	2.18E-13	2.09E-13	2.00E-13
3.16	2.23E-13	2.18E-13	2.09E-13	2.00E-13
5	2.23E-13	2.18E-13	2.09E-13	2.00E-13
5.62	2.23E-13	2.18E-13	2.09E-13	2.00E-13
10	2.23E-13	2.18E-13	2.09E-13	2.00E-13
31.6	2.23E-13	2.18E-13	2.09E-13	2.00E-13
50	2.23E-13	2.18E-13	2.09E-13	2.00E-13
100	2.23E-13	2.18E-13	2.09E-13	2.00E-13
1000	2.23E-13	2.18E-13	2.09E-13	2.00E-13
P (bar)	T = 310 K	T = 311 K	T = 312 K	T = 320 K
0.00533	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.00666	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.00679	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0132	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0133	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.02	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0268	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0316	1.68E-13	1.65E-13	1.62E-13	1.38E-13

0.0333	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.04	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0401	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0533	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.0666	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.08	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.1	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.107	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.133	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.134	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.178	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.316	1.68E-13	1.65E-13	1.62E-13	1.38E-13
0.562	1.68E-13	1.65E-13	1.62E-13	1.38E-13
1	1.68E-13	1.65E-13	1.62E-13	1.38E-13
1.01	1.68E-13	1.65E-13	1.62E-13	1.38E-13
1.78	1.68E-13	1.65E-13	1.62E-13	1.38E-13
2	1.68E-13	1.65E-13	1.62E-13	1.38E-13
3.16	1.68E-13	1.65E-13	1.62E-13	1.38E-13
5	1.68E-13	1.65E-13	1.62E-13	1.38E-13
5.62	1.68E-13	1.65E-13	1.62E-13	1.38E-13
10	1.68E-13	1.65E-13	1.62E-13	1.38E-13
31.6	1.68E-13	1.65E-13	1.62E-13	1.38E-13
50	1.68E-13	1.65E-13	1.62E-13	1.38E-13
100	1.68E-13	1.65E-13	1.62E-13	1.38E-13
1000	1.68E-13	1.65E-13	1.62E-13	1.38E-13
P (bar)	T = 330 K	T = 340 K	T = 350 K	
0.00533	1.15E-13	9.67E-14	8.24E-14	
0.00666	1.15E-13	9.67E-14	8.24E-14	
0.00679	1.15E-13	9.67E-14	8.24E-14	
0.0132	1.15E-13	9.67E-14	8.24E-14	
0.0133	1.15E-13	9.67E-14	8.24E-14	
0.02	1.15E-13	9.67E-14	8.24E-14	
0.0268	1.15E-13	9.67E-14	8.24E-14	
0.0316	1.15E-13	9.67E-14	8.24E-14	
0.0333	1.15E-13	9.67E-14	8.24E-14	
0.04	1.15E-13	9.67E-14	8.24E-14	
0.0401	1.15E-13	9.67E-14	8.24E-14	
0.0533	1.15E-13	9.67E-14	8.24E-14	
0.0666	1.15E-13	9.67E-14	8.24E-14	
0.08	1.15E-13	9.67E-14	8.24E-14	
0.1	1.15E-13	9.67E-14	8.24E-14	
0.107	1.15E-13	9.67E-14	8.24E-14	
0.133	1.15E-13	9.67E-14	8.24E-14	

0.134	1.15E-13	9.67E-14	8.24E-14	
0.178	1.15E-13	9.67E-14	8.24E-14	
0.316	1.15E-13	9.67E-14	8.24E-14	
0.562	1.15E-13	9.67E-14	8.24E-14	
1	1.15E-13	9.67E-14	8.24E-14	
1.01	1.15E-13	9.67E-14	8.24E-14	
1.78	1.15E-13	9.67E-14	8.24E-14	
2	1.15E-13	9.67E-14	8.24E-14	
3.16	1.15E-13	9.67E-14	8.24E-14	
5	1.15E-13	9.67E-14	8.24E-14	
5.62	1.15E-13	9.67E-14	8.24E-14	
10	1.15E-13	9.67E-14	8.24E-14	
31.6	1.15E-13	9.67E-14	8.24E-14	
50	1.15E-13	9.67E-14	8.24E-14	
100	1.15E-13	9.67E-14	8.24E-14	
1000	1.15E-13	9.67E-14	8.24E-14	

[a]The high-pressure limit rate constants were done by the dual-level method with W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ for the high level and M11-L/MG3S for the low-level. The pressure-dependent rate constants were done using SS-QRRK/SCT for the tight TS.

Table S3. The tunneling transmission coefficient (κ_{TSA}, $unitless$), recrossing transmission coefficient (Γ_{TSA}, unitless), conventional transition state theory rate constant ($k^{\ddagger}_{TSA}$, cm^3 molecule^{-1} s^{-1}), and CVT/SCT rate constant ($k^{CVT/SCT}_{TSA}$, cm^3 molecule^{-1} s^{-1}), each calculated using only transition state TSA. The transmission coefficients are calculated at the lower level, the conventional transition state theory rate constant is calculated at the higher level, and the CVT/SCT rate constant is the dual-level result.

T (K)	κ_{TSA}[a]	Γ_{TSA}[b]	$k^{\ddagger}_{TSA}$[c]	$k^{CVT/SCT}_{TSA}$[d]
190	1.03	8.98×10^{-1}	1.22×10^{-8}	1.12×10^{-8}
200	1.02	8.97×10^{-1}	6.34×10^{-9}	5.83×10^{-9}
210	1.02	8.97×10^{-1}	3.54×10^{-9}	3.24×10^{-9}
220	1.02	8.96×10^{-1}	2.09×10^{-9}	1.91×10^{-9}
230	1.02	8.96×10^{-1}	1.30×10^{-9}	1.19×10^{-9}
240	1.02	8.95×10^{-1}	8.49×10^{-10}	7.73×10^{-10}
250	1.02	8.95×10^{-1}	5.75×10^{-10}	5.22×10^{-10}
260	1.01	8.95×10^{-1}	4.03×10^{-10}	3.66×10^{-10}
270	1.01	8.94×10^{-1}	2.91×10^{-10}	2.64×10^{-10}
273	1.01	8.94×10^{-1}	2.65×10^{-10}	2.40×10^{-10}
280	1.01	8.94×10^{-1}	2.16×10^{-10}	1.95×10^{-10}
290	1.01	8.94×10^{-1}	1.64×10^{-10}	1.48×10^{-10}
298	1.01	8.94×10^{-1}	1.34×10^{-10}	1.21×10^{-10}
300	1.01	8.94×10^{-1}	1.27×10^{-10}	1.15×10^{-10}
310	1.01	8.93×10^{-1}	1.01×10^{-10}	9.10×10^{-11}
320	1.01	8.93×10^{-1}	8.12×10^{-11}	7.33×10^{-11}
330	1.01	8.93×10^{-1}	6.65×10^{-11}	5.99×10^{-11}
340	1.01	8.93×10^{-1}	5.52×10^{-11}	4.97×10^{-11}
350	1.01	8.93×10^{-1}	4.64×10^{-11}	4.18×10^{-11}

[a] The M11-L/MG3S tunneling transmission coefficient calculated by the small-curvature tunneling approximation

[b] The M11-L/MG3S recrossing transmission coefficient calculated by $\Gamma_{TSA} = \dfrac{k^{CVT}_{TSA}}{k^{\ddagger}_{TSA}}$, where k^{CVT}_{TSA} and $k^{\ddagger}_{TSA}$ are respectively the canonical variational transition state theory rate constant and the conventional transition state theory rate constant

[c] The W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ conventional transition state theory rate constant

[d] $k^{CVT/SCT}_{TSA} = \kappa_{TSA}\Gamma_{TSA}k^{\ddagger}_{TSA}$

Table S4. The tunneling transmission coefficient (κ_{TSB}, $unitless$), recrossing transmission coefficient (Γ_{TSB}, unitless), conventional transition state theory rate constant ($k^{\ddagger}_{TSB}$, cm^3 molecule^{-1} s^{-1}), and CVT/SCT rate constant ($k^{CVT/SCT}_{TSB}$, cm^3 molecule^{-1} s^{-1}), each calculated using only transition state TSB. The transmission coefficients are calculated at the lower level, the conventional transition state theory rate constant is calculated at the higher level, and the CVT/SCT rate constant is the dual-level result.

T (K)	κ_{TSB}[a]	Γ_{TSB}[b]	$k^{\ddagger}_{TSB}$[c]	$k^{CVT/SCT}_{TSB}$[d]
190	1.49	9.83×10^{-1}	9.07×10^{-12}	1.33×10^{-11}
200	1.43	9.83×10^{-1}	5.24×10^{-12}	7.37×10^{-12}
210	1.38	9.82×10^{-1}	3.19×10^{-12}	4.34×10^{-12}
220	1.34	9.81×10^{-1}	2.05×10^{-12}	2.69×10^{-12}
230	1.31	9.80×10^{-1}	1.37×10^{-12}	1.75×10^{-12}
240	1.28	9.79×10^{-1}	9.46×10^{-13}	1.18×10^{-12}
250	1.25	9.79×10^{-1}	6.77×10^{-13}	8.30×10^{-13}
260	1.23	9.78×10^{-1}	4.99×10^{-13}	6.00×10^{-13}
270	1.21	9.77×10^{-1}	3.76×10^{-13}	4.45×10^{-13}
273	1.21	9.77×10^{-1}	3.48×10^{-13}	4.09×10^{-13}
280	1.19	9.76×10^{-1}	2.91×10^{-13}	3.39×10^{-13}
290	1.18	9.75×10^{-1}	2.29×10^{-13}	2.64×10^{-13}
298	1.17	9.74×10^{-1}	1.92×10^{-13}	2.19×10^{-13}
300	1.17	9.74×10^{-1}	1.84×10^{-13}	2.09×10^{-13}
310	1.16	9.73×10^{-1}	1.50×10^{-13}	1.69×10^{-13}
320	1.14	9.72×10^{-1}	1.24×10^{-13}	1.38×10^{-13}
330	1.14	9.71×10^{-1}	1.04×10^{-13}	1.15×10^{-13}
340	1.13	9.70×10^{-1}	8.86×10^{-14}	9.69×10^{-14}
350	1.12	9.70×10^{-1}	7.61×10^{-14}	8.26×10^{-14}

[a] The M11-L/MG3S tunneling transmission coefficient calculated by the small-curvature tunneling approximation

[b] The M11-L/MG3S recrossing transmission coefficient calculated by $\Gamma_{TSB} = \frac{k^{CVT}_{TSB}}{k^{\ddagger}_{TSB}}$, where k^{CVT}_{TSB} and $k^{\ddagger}_{TSB}$ are respectively the canonical variational transition state theory rate constant and the conventional transition state theory rate constant

[c] The W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ conventional transition state theory rate constant

$$_{d}k_{TSB}^{CVT/SCT} = \kappa_{TSB}\Gamma_{TSB}k_{TSB}^{\ddagger}$$

Table S5. The forward-reaction Arrhenius activation energies (kcal mol^{-1}) for the $CH_2OO + CH_3C(O)CH_3$ reaction based on the local slope at a given temperature of an Arrhenius plot of the fit to the rate constant (see eqns (4) and (5)).

T /K	E_a /kcal mol^{-1}
190	−4.46
200	−4.43
210	−4.4
220	−4.36
230	−4.31
240	−4.27
250	−4.22
252	−4.22
254	−4.21
256	−4.2
258	−4.19
260	−4.18
263	−4.16
270	−4.13
273	−4.12
280	−4.08
283	−4.07
290	−4.04
293	−4.02
294	−4.02
297	−4.00
298	−4.00
300	−3.99
302	−3.98
310	−3.94
311	−3.93
312	−3.93
320	−3.89
330	−3.84
340	−3.79
350	−3.75

Table S6. The value of ν at concentration CH_2OO is 5×10^4 molecule cm^{-3} and concentration OH is as follows (molecule cm^{-3}).

T/K	[OH] = 1×10^4	[OH] = 1×10^5	[OH] = 1×10^6
200	245.33	24.53	2.45
220	96.07	9.61	0.96
240	42.14	4.21	0.42
260	21.39	2.14	0.21
280	10.56	1.06	0.11
298	6.06	0.61	0.06
300	5.81	0.58	0.06
320	3.29	0.33	0.03
340	2.01	0.20	0.02

Table S7. The value of ν at concentration CH_2OO is 5×10^5 molecule cm^{-3} and concentration OH is as follows (molecule cm^{-3}).

T/K	[OH] = 1×10^4	[OH] = 1×10^5	[OH] = 1×10^6
200	2453.33	245.33	24.53
220	960.71	96.07	9.61
240	421.43	42.14	4.21
260	213.93	21.39	2.14
280	105.63	10.56	1.06
298	60.56	6.06	0.61
300	58.06	5.81	0.58
320	32.86	3.29	0.33
340	20.15	2.01	0.20

Table S8. The Cartesian coordinates (Å) of the optimized geometries (which are also used for frequency calculations) by DF-CCSD(T)-F12b/jun-cc-pVDZ.

CH_2OO	C	-1.0671982554	0.2090688552	-0.0000127752
	H	-1.9805889031	-0.3837516053	0.0002305376
	H	-0.9970848188	1.2991181620	0.0003459231
	O	0.0114263246	-0.4726660019	-0.0000440799
	O	1.1769796527	0.1924535899	0.0000253944
$CH_3C(O)CH_3$	C	-0.0000004341	0.1843485513	-0.0000018776
	C	-1.2885068468	-0.6120515884	0.0313697027
	H	-2.1470584460	0.0664659834	0.1002876761
	H	-1.3680872949	-1.2232997228	-0.8815295317
	H	-1.2839205629	-1.3039061568	0.8880768871
	C	1.2885155831	-0.6120362856	-0.0313674219
	H	1.2839376760	-1.3038973257	-0.8880694244
	H	2.1470590034	0.0664911214	-0.1002904488
	H	1.3681033635	-1.2232766235	0.8815363938
	O	-0.0000077912	1.4042193067	-0.0000065154
CA	C	1.8503680420	-1.2164512977	0.1461775342
	O	2.3093110077	-0.1865369153	-0.4225073634
	O	2.3991913637	0.9533354571	0.3356041923
	H	1.5847074124	-1.1637925366	1.2031273054
	H	1.7655944594	-2.0994094974	-0.4869885291
	O	-0.8095644454	-1.0109718942	0.1039000815
	C	-1.5027740322	-0.0043706733	0.0096483613
	C	-0.9061987020	1.3808265873	-0.0629418344
	H	-1.0528944985	1.7698718714	-1.0844156790
	H	-1.4439042603	2.0581920718	0.6185106776
	H	0.1674246473	1.3692877270	0.1702985013
	C	-3.0118788908	-0.1039715424	-0.0434471942
	H	-3.4321494086	0.3278981895	0.8789172683
	H	-3.4035335165	0.4855043421	-0.8863885977
	H	-3.3208761781	-1.1522158893	-0.1330107242

TSA	C	-2.0393275856	-1.0074557243	-0.4188731896
	O	-2.1229867148	-0.2188195591	0.5667626669
	O	-1.9887843796	1.1142154777	0.3105246620
	H	-1.8895218377	-0.5932801262	-1.4171280765
	H	-2.1175096413	-2.0659769141	-0.1717652297
	O	0.6470938345	-0.9789259906	-0.4962174016
	C	1.3997317128	-0.0719435855	-0.1615471468
	C	1.1722422550	1.3564157365	-0.5983319236
	H	0.1242263608	1.5001393301	-0.8866152816
	H	1.4354310587	2.0571945191	0.2073969352
	H	1.8372567656	1.5640010807	-1.4535021915
	C	2.6135889251	-0.3409574936	0.6997628246
	H	3.5039831437	0.1400909761	0.2664766071
	H	2.4497456852	0.1095169245	1.6920231789
	H	2.7742804175	-1.4204166512	0.8069285660
CB	C	2.0996120123	0.5939720054	-0.4488543544
	O	1.8522426511	-0.2494164390	0.4623893855
	O	1.0400947901	-1.2924423123	0.1280504058
	H	1.6967164332	0.4308045411	-1.4493825101
	H	2.7213946744	1.4337470472	-0.1373853154
	O	-0.4542958598	1.2661096346	-0.5194711254
	C	-1.1199041681	0.3396157157	-0.0652596075
	C	-1.4136606843	0.2289273432	1.4139159462
	H	-2.5037393414	0.2285646116	1.5753012793
	H	-1.0123692870	-0.7228027846	1.7912090836
	H	-0.9585220425	1.0700177164	1.9516148304
	C	-1.7515414629	-0.6975019040	-0.9646602844
	H	-1.5922727843	-1.7046090389	-0.5550628178
	H	-2.8377064021	-0.5120081987	-1.0097173621
	H	-1.3280335287	-0.6278569376	-1.9736915538

TSB	C	1.8566909451	-0.5314618177	-0.3738767006
	O	1.6607772051	0.5760148763	0.2195591136
	O	0.6590699938	0.4704486406	1.1695821118
	H	1.5590899387	-1.4598063444	0.1118309739
	H	2.5254946744	-0.4783466693	-1.2352608552
	O	-0.1185882720	-0.5799516540	-1.1731467964
	C	-0.8604421176	-0.1250876443	-0.2671538306
	C	-1.4376989406	1.2649395015	-0.4155631762
	H	-2.3142240343	1.1977870562	-1.0826317000
	H	-1.7553020561	1.6786403067	0.5500709562
	H	-0.6944593283	1.9241454008	-0.8817970854
	C	-1.5272537568	-1.0614743012	0.7136645488
	H	-1.6769812851	-0.5777558117	1.6881947774
	H	-2.5131546799	-1.3404870240	0.3038868791
	H	-0.9274332862	-1.9726275155	0.8339477837
P	C	1.5931441024	0.4213670418	0.4576635607
	H	2.3309816244	0.0321228292	1.1721389726
	H	1.8702646440	1.4142550830	0.0646868408
	O	1.4946283661	-0.5148033792	-0.5920900223
	O	0.2214278141	-0.0743337918	-1.1531134134
	C	-0.5939247791	0.0019386382	0.0270943614
	C	-1.6576380111	1.0446510648	-0.2530586087
	H	-1.1827057273	2.0067610341	-0.4858682088
	H	-2.2831073013	0.7280723399	-1.1002762616
	H	-2.2930744864	1.1581428006	0.6365545423
	C	-1.1356298922	-1.3624612163	0.4147827627
	H	-1.8479373661	-1.7140148625	-0.3458881250
	H	-0.3060839825	-2.0772516233	0.4963526430
	H	-1.6456562077	-1.2922825521	1.3864844654
	O	0.3091682029	0.4597035937	1.0448294910

Table S9. The Cartesian coordinates (Å) of the optimized geometries (which are also used for frequency calculations) by B3LYP/MG3S.

CH_2OO	C	-1.06859300	0.20088900	0.00011700
	H	-1.97492500	-0.38738700	0.00009300
	H	-1.02501000	1.28316200	0.00026500
	O	-0.00161800	-0.45705700	-0.00006700
	O	1.17805500	0.19441900	-0.00006600
$CH_3C(O)CH_3$	C	0.00000000	0.00000000	0.18437600
	O	0.00000000	0.00000000	1.39389100
	C	0.00000000	1.28825600	-0.61107900
	H	0.87697500	1.33149700	-1.26036700
	H	-0.87600600	1.33083100	-1.26170600
	H	-0.00078900	2.14260200	0.05985900
	C	0.00000000	-1.28825600	-0.61107900
	H	-0.87697500	-1.33149700	-1.26036700
	H	0.87600600	-1.33083100	-1.26170600
	H	0.00078900	-2.14260200	0.05985900
CA	C	1.86941800	-1.13583200	0.13884200
	O	2.32029000	-0.12950700	-0.44501400
	O	2.38280800	1.05073200	0.25393800
	H	1.58514100	-1.07123900	1.17955500
	H	1.81009200	-2.03663100	-0.45500900
	O	-0.80311900	-1.03969000	0.08865100
	C	-1.51934800	-0.05954200	0.01213100
	C	-0.96861200	1.34189600	-0.04235000
	H	-1.14342000	1.74992900	-1.04180100
	H	-1.50614200	1.98917400	0.65308400
	H	0.10003400	1.36562100	0.16629800
	C	-3.02297100	-0.20727000	-0.03628300
	H	-3.45806000	0.21183200	0.87390900
	H	-3.43872000	0.35803100	-0.87192500
	H	-3.29968100	-1.25450900	-0.11873700

TSA	C	2.09363500	-0.84651000	0.46800000
	O	2.13880700	-0.15414700	-0.56974200
	O	1.85552700	1.17771300	-0.47921100
	H	1.85418700	-0.38334100	1.41469200
	H	2.29693900	-1.89957200	0.33415500
	O	-0.64464000	-0.98719800	0.62183800
	C	-1.40373300	-0.14596100	0.18315600
	C	-1.35669700	1.29083000	0.64124400
	H	-0.38955200	1.51736200	1.07904100
	H	-1.55415000	1.97602800	-0.18244800
	H	-2.14256400	1.44286800	1.38684200
	C	-2.45476700	-0.50223100	-0.84158800
	H	-3.42795100	-0.09787500	-0.55812100
	H	-2.18825500	-0.04336500	-1.79677600
	H	-2.51683500	-1.57982100	-0.96533800
CB	C	2.12325000	-0.79288900	-0.02631900
	O	1.98809200	0.43159900	-0.23150000
	O	1.22383100	1.15513100	0.63601300
	H	1.65655200	-1.25195500	0.83378300
	H	2.71734600	-1.32078700	-0.75946800
	O	-0.55841900	-1.29344000	-0.37200100
	C	-1.23045800	-0.30814400	-0.13147700
	C	-1.54954200	0.71171100	-1.19788300
	H	-2.62714300	0.73247300	-1.37723700
	H	-1.25321900	1.70573700	-0.86350500
	H	-1.03483300	0.46545300	-2.12243100
	C	-1.81373000	-0.06294300	1.23910400
	H	-1.34763600	0.82442400	1.66891400
	H	-2.88642800	0.12806300	1.17292000
	H	-1.62979300	-0.91614000	1.88638000

TSB	C	-1.83098600	0.54985200	-0.36601600
	O	-1.69997500	-0.58035400	0.17933900
	O	-0.71472500	-0.58100000	1.15578000
	H	-1.52965400	1.44248700	0.15832000
	H	-2.47324100	0.57139400	-1.23641200
	O	0.11300700	0.53704900	-1.16530300
	C	0.87704900	0.13679200	-0.26263100
	C	1.55465900	-1.20264700	-0.41185800
	H	2.44993000	-1.06557400	-1.02621700
	H	1.85846500	-1.61504200	0.54680700
	H	0.89473400	-1.89870700	-0.92205800
	C	1.45772600	1.10177500	0.73971500
	H	1.62829400	0.62776400	1.70330900
	H	2.42222200	1.45041800	0.35706300
	H	0.81210400	1.96706600	0.86539800
P	C	1.59894300	-0.41811500	-0.46476400
	H	2.32570400	-0.01610900	-1.17012100
	H	1.88522900	-1.41174100	-0.10535400
	O	1.50269600	0.49204300	0.60710400
	O	0.22137700	0.08184800	1.15377700
	C	-0.59805300	-0.00221700	-0.02496500
	C	-1.65588500	-1.05257200	0.25281000
	H	-1.18573500	-2.00406200	0.49019000
	H	-2.28589400	-0.74663300	1.08697300
	H	-2.28372200	-1.17619900	-0.62803800
	C	-1.15633600	1.35665300	-0.41274100
	H	-1.86861400	1.70123900	0.33618200
	H	-0.34748800	2.07942000	-0.49267500
	H	-1.66201100	1.28977800	-1.37519700
	O	0.31224100	-0.45116500	-1.04138100

Table S10. The Cartesian coordinates (Å) of the optimized geometries (which are also used for frequency calculations) by M11-L/MG3S.

CH_2OO	C	-1.05494800	0.20065900	-0.00016800
	H	-1.96977200	-0.37543600	0.00025200
	H	-0.99334700	1.28293100	0.00041800
	O	-0.00394400	-0.45596500	0.00005900
	O	1.16554500	0.19203400	-0.00001600
$CH_3C(O)CHCH_2$	C	-1.72758500	-0.58253200	-0.00015000
	H	-1.78273200	-1.24253200	-0.87572300
	H	-2.58078100	0.09855800	-0.00073000
	H	-1.78333900	-1.24169900	0.87601700
	C	-0.43991200	0.17200800	0.00003100
	C	0.78889500	-0.66129500	0.00013400
	H	0.67294500	-1.74854300	0.00017000
	C	1.98351600	-0.10376000	0.00019600
	H	2.07283300	0.98481200	0.00015500
	H	2.90333300	-0.6874210	0.00029200
	O	-0.39146700	1.36128800	-0.00018100
C2A	C	0.34886000	1.52781000	0.05466500
	H	0.74358700	2.19104900	0.83587200
	H	-0.72830000	1.38694200	0.19144700
	H	0.52703200	2.05756700	-0.89121800
	C	1.10394700	0.24878700	0.05194700
	C	2.57660200	0.37122800	-0.06947000
	H	2.99698200	1.37705000	-0.14735000
	C	3.35051500	-0.69595200	-0.08369700
	H	2.90676200	-1.69064300	-0.00459600
	H	4.43425300	-0.63149900	-0.17247600
	O	0.58167400	-0.82476000	0.13734400
	C	-2.02911900	-1.20544100	0.20840800
	H	-1.80137500	-1.00100700	1.25837200
	H	-1.78265500	-2.13307200	-0.30993100
	O	-2.60840500	-0.35623700	-0.46748500
	O	-2.89840800	0.80162400	0.11373600

TS2A	C	0.45242100	1.67124100	0.43977200
	H	1.16178000	2.33829300	0.94752700
	H	-0.50755100	1.66145300	0.95885000
	H	0.29623800	2.09300400	-0.56145200
	C	1.02838800	0.30641800	0.32347300
	C	2.35191700	0.22388900	-0.34002600
	H	2.79579700	1.15388200	-0.70434000
	C	2.97044300	-0.93116200	-0.48470000
	H	2.50620600	-1.84641400	-0.11126800
	H	3.94248300	-1.01838500	-0.96846700
	O	0.48014700	-0.67513300	0.73219400
	C	-2.14523400	-1.05258700	0.49363600
	H	-2.17039300	-0.44801900	1.40471400
	H	-1.98674800	-2.13156500	0.46776600
	O	-2.28690500	-0.51315400	-0.60309300
	O	-2.44141800	0.79965700	-0.63238400
C2B	C	1.46284100	1.67165300	-0.09637300
	H	2.54764800	1.69399400	0.07956500
	H	1.00090600	2.47959200	0.47482700
	H	1.30811400	1.83292200	-1.16755200
	C	0.93005400	0.35036900	0.33521000
	C	1.26091900	-0.80655900	-0.52739700
	H	1.66832100	-0.60005200	-1.51954300
	C	1.07754200	-2.04111300	-0.10310600
	H	0.67993900	-2.21934000	0.89865200
	H	1.31545300	-2.91146800	-0.71316000
	O	0.33843100	0.20240300	1.37043400
	C	-2.06897100	-0.10385700	0.65994600
	H	-1.90250600	0.86163300	1.14422300
	H	-2.54538100	-0.96797600	1.12916400
	O	-1.73614800	-0.26912000	-0.51400000
	O	-1.10813200	0.74268500	-1.09841600

TS2B	C	-1.16497500	-1.80810900	0.00084600
	H	-1.41878000	-1.94042100	-1.05480000
	H	-2.07414800	-1.99430300	0.58923100
	H	-0.41505200	-2.54583400	0.29652200
	C	-0.67620500	-0.43500500	0.28755000
	C	-1.31396200	0.68477700	-0.41838000
	H	-1.83830500	0.45686200	-1.34843500
	C	-1.24805800	1.91508200	0.05269200
	H	-0.72962300	2.11555400	0.99209800
	H	-1.70460000	2.76018000	-0.46017600
	O	0.02780400	-0.21737600	1.27579300
	C	1.84765500	0.16465800	0.56753900
	H	2.01401400	-0.88792900	0.80285000
	H	2.24089300	0.97725900	1.18770300
	O	1.51669500	0.49421700	-0.58577900
	O	0.86285900	-0.53556400	-1.18332400
P2	C	-1.39466000	-1.05856500	0.32623500
	H	-1.19824700	-1.98251100	-0.25636900
	H	-2.16471100	-1.23666300	1.09367900
	O	-1.83579000	-0.04819400	-0.48517000
	O	-0.60792700	0.26024000	-1.10620700
	C	0.09776100	1.74568500	0.64492500
	H	0.63596300	1.77152100	1.59736800
	H	-0.95883500	1.96171700	0.83201200
	H	0.50896100	2.52146300	-0.00933900
	C	0.22685100	0.38872000	0.01272000
	C	1.61071900	0.09851600	-0.46098400
	H	1.99607900	0.79293700	-1.21212700
	C	2.34767300	-0.88548300	-0.00097000
	H	1.96593300	-1.56724100	0.75904400
	H	3.36319900	-1.05084400	-0.35785000
	O	-0.24108300	-0.57999900	0.89413100
CH_3CHO	C	1.14902700	-0.14648900	-0.00003300
	H	1.69120700	0.23578400	-0.87446400
	H	1.16224600	-1.23944900	-0.00059500
	H	1.69054100	0.23473800	0.87529900
	C	-0.23609700	0.38453100	0.00001700
	H	-0.29236900	1.51308100	-0.00007100
	O	-1.21615100	-0.27155000	-0.00000900

C3A	C	-1.53173700	1.18918600	0.00854700
	H	-1.81484100	1.69510200	-0.92452700
	H	-0.45213500	1.28960000	0.17385300
	H	-2.09186700	1.71003400	0.79656800
	C	-1.98300000	-0.21458100	-0.05595300
	H	-3.09459900	-0.33843000	-0.20145300
	O	-1.29078700	-1.17327200	0.02898300
	C	1.37240500	-1.04347100	0.20943300
	H	1.35952100	-1.98762100	-0.33691200
	H	1.07498800	-0.92510500	1.25538200
	O	1.76116000	-0.06576900	-0.42924200
	O	1.76374300	1.11024400	0.18337500
TS3A	C	1.66427000	-0.83747600	0.40154800
	O	1.74392000	0.07230000	-0.42368000
	O	1.33791400	1.27449900	-0.06215100
	H	1.28050600	-0.62977800	1.40432200
	H	1.98226900	-1.81856800	0.04561300
	O	-0.99059600	-1.24038400	-0.00719600
	C	-1.79853400	-0.41425000	-0.26811600
	C	-1.82860400	0.96449100	0.25987700
	H	-0.98972700	1.16471400	0.93087900
	H	-1.79046200	1.67143600	-0.57873000
	H	-2.79137200	1.14069200	0.75806100
	H	-2.64390300	-0.65641200	-0.97578200
C3B	C	2.04561900	0.46049000	-0.44857100
	H	1.87111800	1.53733200	-0.36243500
	H	1.89192400	0.13132700	-1.48044200
	H	3.09525100	0.28272400	-0.17475500
	C	1.17912000	-0.28814800	0.49247200
	H	1.17299200	0.11812900	1.53921300
	O	0.60112100	-1.29638000	0.22674300
	C	-1.69195000	-0.57216200	-0.53630900
	H	-2.44145500	-1.33974200	-0.33214800
	H	-1.03651300	-0.55513500	-1.41073900
	O	-1.62990000	0.33008300	0.29955200
	O	-0.68997800	1.24433300	0.12067300

TS3B	C	-1.90430800	0.28877300	0.49377100
	H	-1.57064400	0.03090900	1.50442400
	H	-2.87914700	-0.19290300	0.33168200
	H	-2.04836500	1.37040000	0.41839300
	C	-0.95608100	-0.21037800	-0.53186600
	H	-1.10172900	0.20848500	-1.55427200
	O	-0.29419600	-1.22508900	-0.39334500
	C	1.38342800	-0.53753800	0.61302900
	H	2.10916100	-1.35149200	0.53279400
	H	0.72301400	-0.41170300	1.47254600
	O	1.52429100	0.38535000	-0.20518300
	O	0.47358900	1.22738500	-0.17086800
P3	C	-2.01113100	-0.06959400	0.18753900
	H	-2.59392600	0.83185900	-0.02320400
	H	-1.94543400	-0.21445200	1.27033300
	H	-2.53457500	-0.92389600	-0.24992000
	C	-0.65021700	0.03606300	-0.40153600
	H	-0.67998200	0.19924200	-1.50190500
	O	0.11802100	-1.08573900	-0.12870000
	C	1.34764300	-0.59190200	0.23664800
	H	2.16899800	-1.09334700	-0.30343500
	H	1.49009900	-0.69160100	1.33276900
	O	1.34835700	0.72174100	-0.15921100
	O	0.03075300	1.06959700	0.20534300
syn-CH_3CHOO	C	0.45815900	0.69934600	0.00032200
	H	0.77797700	1.74489400	0.00008400
	O	-0.77857300	0.56794400	-0.00022300
	O	-1.22463600	-0.67673500	0.00011200
	C	1.32713700	-0.45305400	-0.00009900
	H	2.38228600	-0.17762800	-0.00149800
	H	1.07802200	-1.08697400	0.86432900
	H	1.07562300	-1.08771300	-0.86336100
$CH_3C(O)CH_3$	C	0.00000000	0.00000000	0.19339800
	O	0.00000000	0.00000000	1.38038500
	C	0.00000000	-1.26621400	-0.60456100
	H	-0.93047700	-1.34735100	-1.18100200
	H	0.81188500	-1.26787300	-1.34214600
	H	0.09240500	-2.13645700	0.04878000
	C	0.00000000	1.26621400	-0.60456100
	H	0.93047700	1.34735100	-1.18100200
	H	-0.81188500	1.26787300	-1.34214600
	H	-0.09240500	2.13645700	0.04878000

C4A	C	1.73433900	-0.66819000	-0.56130900
	H	1.50911500	-1.24608200	-1.46187100
	O	1.82023600	0.55045600	-0.77281500
	O	2.06832700	1.30593600	0.30347500
	C	1.93659400	-1.22377000	0.75582000
	H	1.82222100	-2.30817200	0.76414500
	H	2.92763200	-0.91690700	1.12122500
	H	1.23093400	-0.74719200	1.44952500
	C	-1.76923600	-0.08377400	-0.00682800
	O	-1.00419200	-0.97351800	-0.22037400
	C	-3.24717700	-0.30485200	-0.03225600
	H	-3.64297800	-0.22899100	0.98896800
	H	-3.75775400	0.47476600	-0.61001400
	H	-3.49058300	-1.29145600	-0.43271300
	C	-1.32218900	1.30666700	0.29150600
	H	-1.44497600	1.91258400	-0.61707200
	H	-1.95523300	1.77841500	1.05206300
	H	-0.26732600	1.35356900	0.58185700
TS4A	C	-1.88023900	-0.71569900	0.43972700
	H	-1.83013400	-1.61649500	1.05817000
	O	-1.52564900	0.30638000	1.04610600
	O	-1.53488700	1.43361900	0.33560100
	C	-2.29812400	-0.67088800	-0.94054900
	H	-2.62089600	-1.64747100	-1.30323700
	H	-3.08700800	0.08687300	-1.05110100
	H	-1.45846500	-0.29055200	-1.53977200
	C	1.69302400	-0.19418200	-0.18600400
	O	0.85165300	-1.02452500	-0.33685400
	C	2.92668000	-0.46383500	0.61349400
	H	3.82656900	-0.12280900	0.08773100
	H	2.88564600	0.11503500	1.54545900
	H	3.01335800	-1.52466500	0.85920100
	C	1.59021000	1.16748700	-0.78684600
	H	1.97916900	1.93942700	-0.11369600
	H	2.21741600	1.19972700	-1.68863200
	H	0.55610700	1.39984100	-1.05188000

C4B	C	1.93628200	0.32114900	-0.50680300
	H	2.32117700	0.78672800	-1.41949000
	O	1.24141600	1.09501600	0.16891100
	O	0.71720000	0.57436500	1.28109900
	C	2.19750900	-1.03366300	-0.08594500
	H	2.88788900	-1.54485900	-0.75779500
	H	2.56951700	-1.01659200	0.94843700
	H	1.23829700	-1.56905800	-0.03199300
	C	-1.42729900	-0.24280200	-0.34442900
	O	-0.71975200	-0.66075100	-1.20970500
	C	-1.96331200	1.15020700	-0.36180600
	H	-3.04498700	1.16380300	-0.18082600
	H	-1.49927100	1.71223200	0.45831900
	H	-1.73986500	1.64203900	-1.31156700
	C	-1.85791300	-1.08671400	0.80984300
	H	-1.74337300	-0.54402600	1.75407500
	H	-2.92428300	-1.33014200	0.70743200
	H	-1.28761600	-2.01822900	0.84581300
TS4B	C	-1.58095600	-0.42923900	-0.36922100
	H	-2.05103800	-0.99841800	-1.18374900
	O	-0.93110500	-1.18410800	0.39357500
	O	-0.11199900	-0.47299600	1.21344100
	C	-2.07911900	0.89740700	-0.03171400
	H	-2.11431400	1.52305400	-0.92511600
	H	-3.11097300	0.77711900	0.33567900
	H	-1.46710700	1.36336500	0.73844900
	C	1.00022200	0.20558800	-0.28229400
	O	0.14567300	0.36247400	-1.15946500
	C	1.90470800	-0.98240600	-0.35163700
	H	2.45132100	-1.15500400	0.57937200
	H	1.33061600	-1.87752000	-0.60820200
	H	2.63354100	-0.81928000	-1.15808000
	C	1.51182800	1.38513400	0.47934100
	H	0.73595500	2.15009200	0.57257200
	H	1.87744700	1.10691800	1.47260800
	H	2.35390600	1.82780600	-0.07078800

P4	C	-1.26055200	-0.35112600	-0.44786500
	H	-1.67295000	-1.08887200	-1.16433200
	O	-0.78493200	-1.10415200	0.61239200
	O	0.17322400	-0.21133400	1.13516000
	C	-2.28386700	0.66180100	-0.04252900
	H	-2.55801900	1.28617200	-0.89867400
	H	-3.18744800	0.17164900	0.33457100
	H	-1.87712400	1.30861300	0.74186400
	C	0.86807700	0.11501500	-0.02507800
	O	-0.13970900	0.25410600	-0.97802000
	C	1.81513400	-0.97791600	-0.43429800
	H	2.24943300	-0.75589700	-1.41414500
	H	2.62794600	-1.08303900	0.29203700
	H	1.27991200	-1.92926400	-0.50266300
	C	1.53398800	1.43259500	0.22055400
	H	2.28358500	1.34817400	1.01339700
	H	2.03813100	1.76843900	-0.69007100
	H	0.79118400	2.18285600	0.50705800
anti-CH_3CHOO	C	-0.36746200	0.41182100	0.00011900
	H	-0.10045400	1.47717200	-0.00026000
	O	0.56919400	-0.39832700	0.00001600
	O	1.80361500	0.06491800	-0.00003400
	C	-1.72932600	-0.10122300	-0.00001000
	H	-2.28348600	0.26140300	0.87634900
	H	-2.28275000	0.25925700	-0.87773900
	H	-1.73504900	-1.19414900	0.00114500
C5A	C	1.75409200	-0.12578900	-0.05774400
	O	0.86461700	-0.90461500	-0.22336000
	C	1.55316200	1.34764700	-0.12056300
	H	2.10989900	1.85724200	0.67494900
	H	1.98211100	1.71616100	-1.06298800
	H	0.49222000	1.62167400	-0.08474400
	C	3.14671500	-0.59024900	0.22285900
	H	3.87944800	-0.05072700	-0.38846600
	H	3.39965400	-0.36173600	1.26644900
	H	3.24252500	-1.66688400	0.06533000
	C	-1.80807600	-0.35729300	-0.35761000
	H	-1.46428200	-0.09831300	-1.36720800
	O	-1.97601700	0.57381500	0.43486800
	O	-1.70398100	1.81205300	0.00246700
	C	-2.08823100	-1.71417400	0.08436300
	H	-2.86311000	-2.17234100	-0.54437600
	H	-1.18548300	-2.32763700	-0.02534500
	H	-2.41589700	-1.72831400	1.12676800

TS5A	C	1.69784100	-0.21089300	-0.11963200
	O	0.81222800	-0.99501900	-0.28315400
	C	1.61062400	1.18633500	-0.63335500
	H	2.44288100	1.81925500	-0.31161900
	H	1.60839900	1.15488100	-1.73023400
	H	0.65341100	1.63240600	-0.32728500
	C	2.94613900	-0.58328400	0.60611700
	H	3.82508600	-0.38321700	-0.01968800
	H	3.06241700	0.05530200	1.49130100
	H	2.93484600	-1.63258800	0.90916800
	C	-1.81253600	-0.21879900	-0.34859800
	H	-1.51412700	0.15310900	-1.33761600
	O	-1.81872900	0.59437200	0.57943900
	O	-1.44613300	1.85187200	0.30774800
	C	-2.19617800	-1.59471100	-0.07805900
	H	-3.03705800	-1.89485400	-0.71658000
	H	-1.35734100	-2.25968700	-0.31940000
	H	-2.47278000	-1.72629600	0.97085900
C5B	C	-1.29384200	0.49010000	0.06680600
	O	-0.36600600	1.25177200	0.07468900
	C	-2.06731400	0.20108300	-1.17582100
	H	-2.25223900	-0.87136800	-1.28660900
	H	-3.04832300	0.69375300	-1.11525900
	H	-1.54303100	0.58018200	-2.05671600
	C	-1.83740800	-0.08481800	1.33309700
	H	-2.63738500	0.57370300	1.70127300
	H	-2.26587600	-1.07992000	1.18861100
	H	-1.05718500	-0.12499300	2.09716300
	C	1.65904600	-0.05330700	-0.41711000
	H	1.21864900	0.14149500	-1.40228700
	O	1.17600700	-0.97810900	0.24320500
	O	0.08525300	-1.56074400	-0.27903200
	C	2.75854400	0.71146200	0.14541300
	H	3.61555100	0.73159500	-0.53851600
	H	2.42843900	1.75151700	0.27162800
	H	3.06522200	0.31356300	1.11549700

TS5B	C	-1.08554300	0.36028100	0.17459900
	O	-0.09091900	0.99154300	0.53063700
	C	-1.80132700	0.72092200	-1.08477800
	H	-2.33073500	-0.13239200	-1.51907900
	H	-2.54496700	1.49982500	-0.86218100
	H	-1.10510200	1.12769700	-1.82418200
	C	-1.87033200	-0.39496300	1.19527000
	H	-2.51107100	0.31073300	1.74332800
	H	-2.51232000	-1.15887800	0.74847000
	H	-1.19387000	-0.86175100	1.91589400
	C	1.47785000	0.04381800	-0.38894800
	H	1.09904500	0.50183300	-1.30779700
	O	1.02128700	-1.07536300	-0.07375400
	O	-0.19426400	-1.26880500	-0.64716100
	C	2.66485600	0.52475200	0.30307600
	H	3.51846000	0.58047500	-0.38293200
	H	2.46702800	1.53994000	0.66242300
	H	2.91168000	-0.11533600	1.15297000
P5	C	0.92208500	0.02892600	0.08919800
	O	-0.18553500	-0.20142100	0.90374100
	C	2.04897200	-0.89185700	0.43994800
	H	2.88167700	-0.77282500	-0.26055600
	H	2.41562500	-0.66540700	1.44537900
	H	1.70891700	-1.93117200	0.41496700
	C	1.28405300	1.48560800	0.14560700
	H	1.48111700	1.78965900	1.17863700
	H	2.17584200	1.69228600	-0.45562800
	H	0.45293600	2.08595900	-0.23671100
	C	-1.23538000	-0.46679700	0.05064500
	H	-1.34263600	-1.56764700	-0.08205100
	O	-0.85186500	0.10229000	-1.14430400
	O	0.48098300	-0.34185700	-1.18331700
	C	-2.49789900	0.16554300	0.51785800
	H	-3.31365400	-0.03561600	-0.18265300
	H	-2.77620400	-0.24335100	1.49275300
	H	-2.36326900	1.24748300	0.61737500

Table S11. Absolute energies in hartrees.

Species	Method	Total energy (a.u.)
CH_2OO	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-189.7223494
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-189.7193694
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-189.4053176
	CBS-QB3	-189.373842
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-189.6822427
	WMS//M11-L/MG3S	-189.6814116
	M11-L/MG3S	-189.5829489
	M06CR/MG3S	-189.4727729
	MN15-L/MG3S	-189.4750307
	M06-2X/MG3S	-189.5654488
$CH_3C(O)CH_3$	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-193.2720245
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-193.2704814
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-192.9275326
	CBS-QB3	-192.901923
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-193.2298872
	WMS//M11-L/MG3S	-193.2289445
	M11-L/MG3S	-193.1751747
	M06CR/MG3S	-193.0129886
	MN15-L/MG3S	-193.0315698
	M06-2X/MG3S	-193.1308427
CA	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0053883
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0010702
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-382.3442834
	CBS-QB3	-382.287675
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-382.9227426
	WMS//M11-L/MG3S	-382.9198481
	M11-L/MG3S	-382.7681605
	M06CR/MG3S	-382.4971124
	MN15-L/MG3S	-382.5198569
	M06-2X/MG3S	-382.7106115
TSA	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0044937
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0001513
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-382.3432226
	CBS-QB3	-382.287067
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-382.9219745
	WMS//M11-L/MG3S	-382.9189373
	M11-L/MG3S	-382.767225
	M06CR/MG3S	-382.4963547
	MN15-L/MG3S	-382.5189631
	M06-2X/MG3S	-382.7093169

CB	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0082139
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0040193
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-382.3465565
	CBS-QB3	-382.29094
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-382.9256983
	WMS//M11-L/MG3S	-382.9226958
	M11-L/MG3S	-382.7709323
	M06CR/MG3S	-382.4999604
	MN15-L/MG3S	-382.5241368
	M06-2X/MG3S	-382.7146208
TSB	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0044879
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0007207
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-382.3437838
	CBS-QB3	-382.288718
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-382.9222644
	WMS//M11-L/MG3S	-382.9197814
	M11-L/MG3S	-382.7670134
	M06CR/MG3S	-382.492531
	MN15-L/MG3S	-382.5196257
	M06-2X/MG3S	-382.7101004
P	W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0784613
	W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-383.0761346
	CCSD(T)-F12a/VTZ-F12//B3LYP/MG3S	-382.4190382
	CBS-QB3	-382.36424
	WMS//DF-CCSD(T)-F12b/jun-cc-pVDZ	-382.9969636
	WMS//M11-L/MG3S	-382.9923594
	M11-L/MG3S	-382.839762
	M06CR/MG3S	-382.5646216
	MN15-L/MG3S	-382.590982
	M06-2X/MG3S	-382.7916825
$CH_3C(O)CHCH_2$	WMS//M11-L/MG3S	-231.3183369
	M11-L/MG3S	-231.2567216
C2A	WMS//M11-L/MG3S	-421.0092832
	M11-L/MG3S	-420.8494615
TS2A	WMS//M11-L/MG3S	-421.008087
	M11-L/MG3S	-420.8483841
C2B	WMS//M11-L/MG3S	-421.0119029
	M11-L/MG3S	-420.8529254
TS2B	WMS//M11-L/MG3S	-421.0099662
	M11-L/MG3S	-420.8488404
P2	WMS//M11-L/MG3S	-421.0772766
	M11-L/MG3S	-420.9160801
CH_3CHO	WMS//M11-L/MG3S	-153.8937342

	M11-L/MG3S	-153.8442977
C3A	WMS//M11-L/MG3S	-343.5843274
	M11-L/MG3S	-343.4368809
TS3A	WMS//M11-L/MG3S	-343.5831945
	M11-L/MG3S	-343.4358659
C3B	WMS//M11-L/MG3S	-343.5872752
	M11-L/MG3S	-343.440046
TS3B	WMS//M11-L/MG3S	-343.5861225
	M11-L/MG3S	-343.4372129
P3	WMS//M11-L/MG3S	-343.6600355
	M11-L/MG3S	-343.512028
syn-CH_3CHOO	WMS//M11-L/MG3S	-229.020728
	M11-L/MG3S	-228.9231196
C4A	WMS//M11-L/MG3S	-422.2604436
	M11-L/MG3S	-422.1076859
TS4A	WMS//M11-L/MG3S	-422.2595716
	M11-L/MG3S	-422.1068489
C4B	WMS//M11-L/MG3S	-422.2632573
	M11-L/MG3S	-422.1107387
TS4B	WMS//M11-L/MG3S	-422.2541486
	M11-L/MG3S	-422.0989088
P4	WMS//M11-L/MG3S	-422.3253557
	M11-L/MG3S	-422.1684496
anti-CH_3CHOO	WMS//M11-L/MG3S	-229.0147786
	M11-L/MG3S	-228.9170142
C5A	WMS//M11-L/MG3S	-422.2571467
	M11-L/MG3S	-422.1036766
TS5A	WMS//M11-L/MG3S	-422.2566387
	M11-L/MG3S	-422.1033779
C5B	WMS//M11-L/MG3S	-422.2604523
	M11-L/MG3S	-422.1075843
TS5B	WMS//M11-L/MG3S	-422.2590748
	M11-L/MG3S	-422.1039683
P5	WMS//M11-L/MG3S	-422.326879
	M11-L/MG3S	-422.1701946

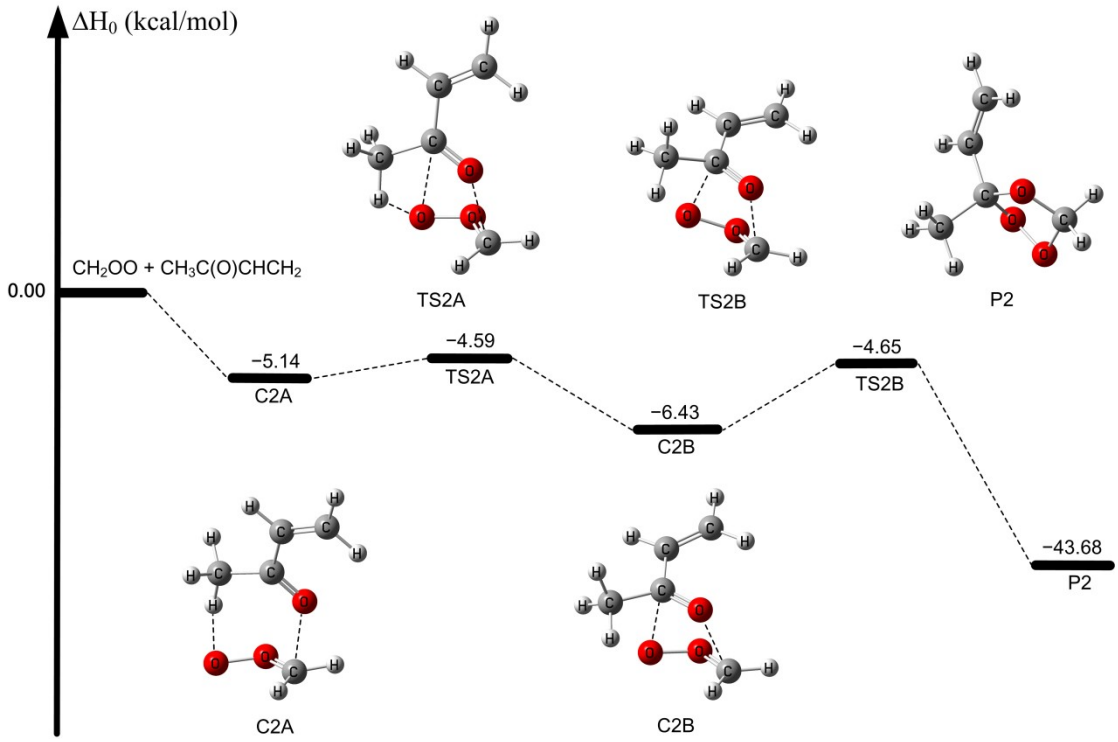

Figure S1. The calculated enthalpy profile for the $CH_2OO + CH_3C(O)CHCH_2$ reaction by WMS//M11-L/MG3S at 0 K.

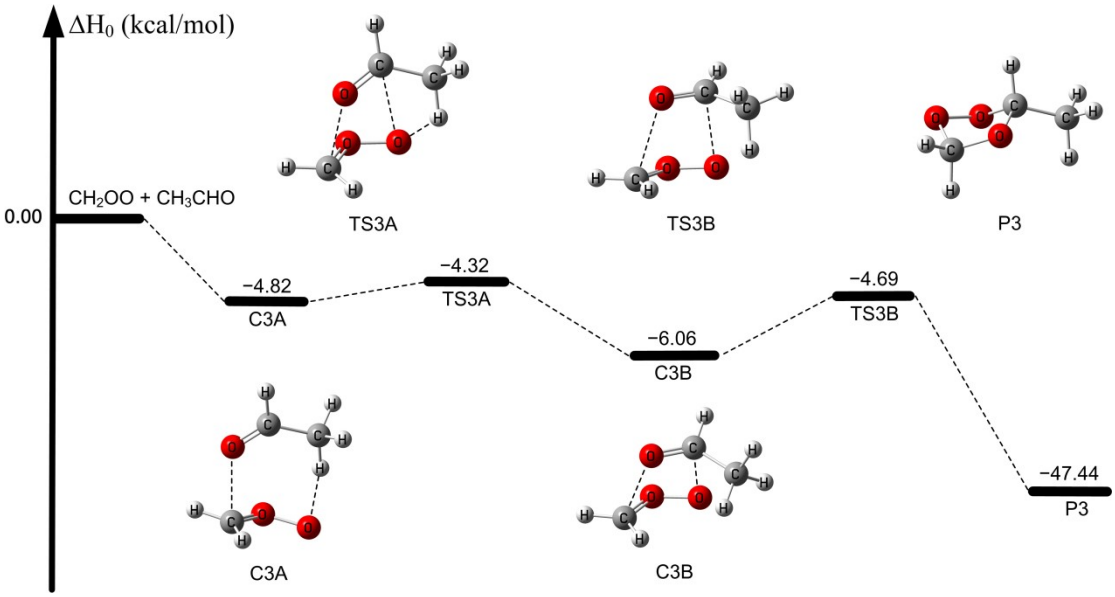

Figure S2. The calculated enthalpy profile for the $CH_2OO + CH_3CHO$ reaction by WMS//M11-L/MG3S at 0 K.

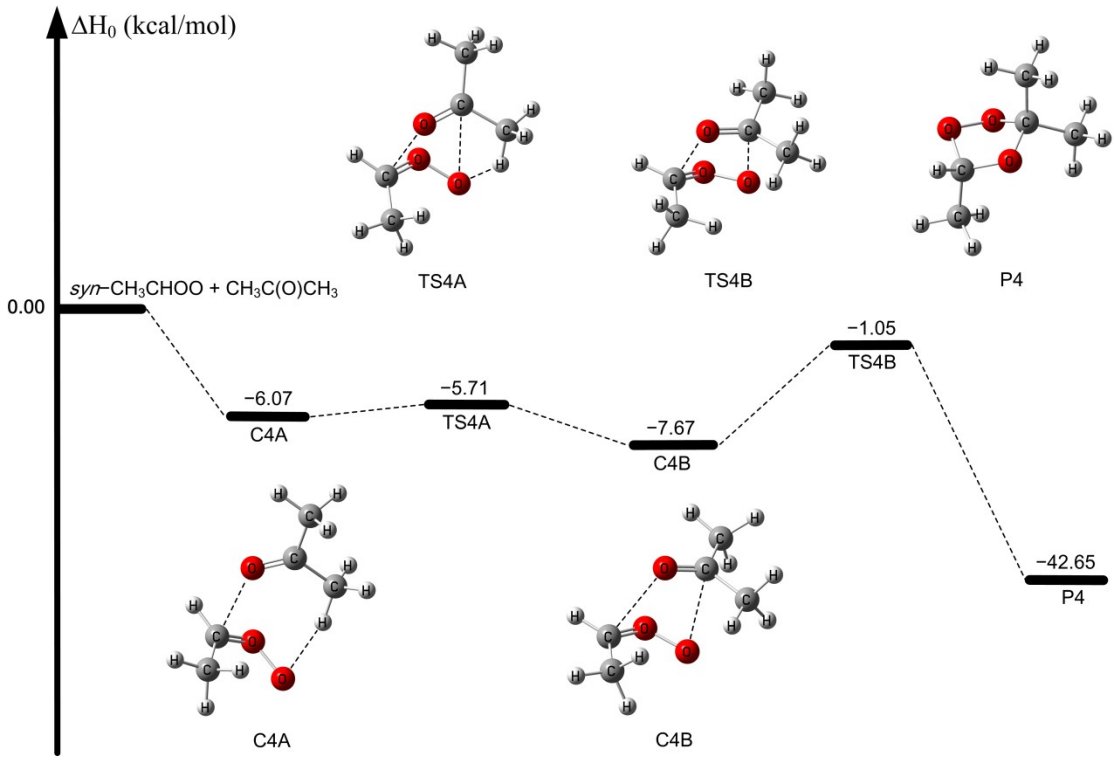

Figure S3. The calculated enthalpy profile for the *syn*-CH_3CHOO + $CH_3C(O)CH_3$ reaction by WMS//M11-L/MG3S at 0 K.

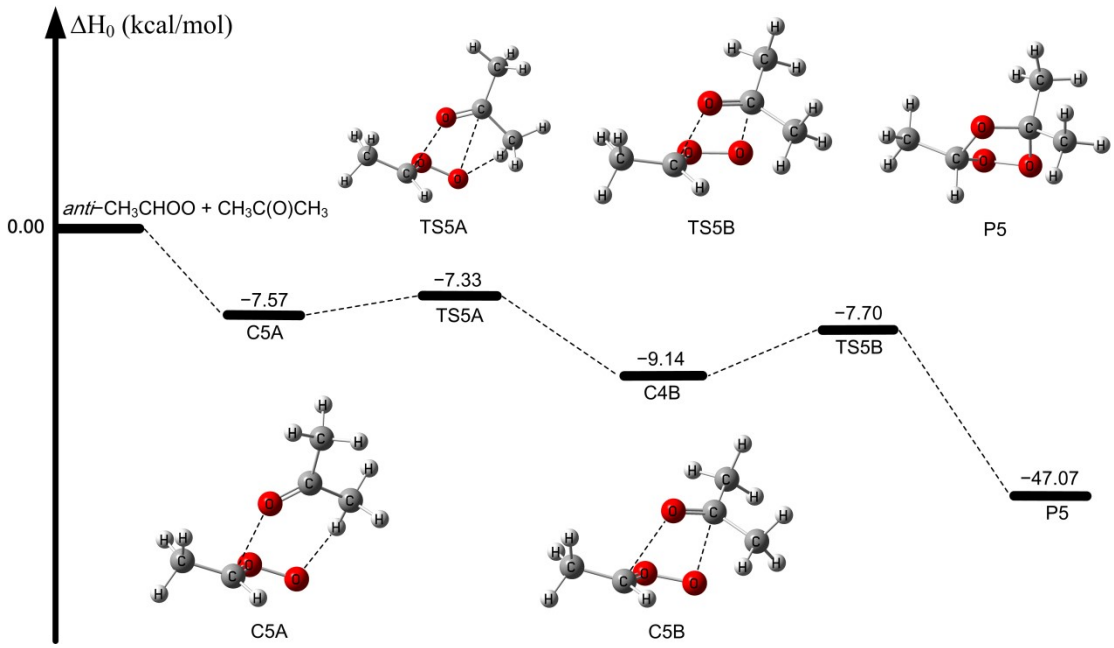

Figure S4. The calculated enthalpy profile for the *anti*-CH_3CHOO + $CH_3C(O)CH_3$ reaction by WMS//M11-L/MG3S at 0 K.