SUPPORTING INFORMATION

Quantitative Kinetics Reveal that Reactions of HO_2 are a Significant Sink for Aldehydes in the Atmosphere and may Initiate the Formation of Highly Oxygenated Molecules via Autoxidation

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S1. Computational details of high-pressure-limit rate coefficients

Reactions R1–R3 are pressure dependent, and the first step in calculating their rate constants is to calculate their high-pressure-limit (HPL) rate constants. The single-state calculations of reaction rates for R1, R2, and R3 are mainly based on passage through transition states TS1A, TS1B, and TS1C, respectively. These are the lowest-energy transition structures for these reactions. Passage through higher-energy conformers of the transition states is accounted for in the multistructural torsional anharmonicity factor. We use a dual-level strategy in which the lower level (LL) is M11-L/MG3S, and the higher level (HL) is CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/MG3S.

The HPL rate coefficients were calculated by the following formula:

$$k_{MS-\overset{DL}{CVT/SCT}} = F_{fwd}^{MS-T}\kappa_{SS-\overset{LL}{SCT}}\Gamma_{SS-\overset{LL}{CVT}}k_{SS-\overset{HL}{TST}} \quad \text{(S1)}$$

where all quantities in this expression are functions of temperature, $k_{MS-\overset{DL}{CVT/SCT}}(T)$ is the rate coefficient of dual-level multistructural canonical variational transition state theory with small-curvature tunneling for the reaction from the conformational ensemble of bimolecular reagents to the conformational ensemble of transition states for this reaction, F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor, which includes the contributions from all the conformational structures of the reactants and the transition states, $\kappa_{SS-\overset{LL}{SCT}}$ is the tunneling coefficient calculated by using ground-state small-curvature tunneling for the lowest-energy transition state from the pre-reactive complex to the corresponding adduct, $\Gamma_{SS-\overset{LL}{CVT},TS1B}$ is the recrossing effect and is equal to $\kappa_{SS-\overset{LL}{CVT}}/\kappa_{SS-\overset{LL}{TST}}$ obtained by using single-structure canonical variational transition state theory without tunneling for the lowest-energy conformers, and $k_{SS-\overset{HL}{TST}}$ is the single-structure conventional transition state theory rate coefficient without tunneling for the lowest-energy conformers.

The HPL rate constants for reactions R4, R5, and R6 (the 1,7-H-shift reactions) are mainly based on passage through transition states TS2A, TS2B, and TS2C, respectively. These are the lowest-energy transition structure for these reactions. Passage through higher-energy conformers of the transition states is accounted for in the multistructural torsional anharmonicity factor. We again use a dual-level strategy in which the lower level (LL) is MN15-L/MG3S for R4-R6, and the higher level (HL) is CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/MG3S. The HPL rate constants are again calculated by eq S1.

S2. Computational details of pressure-dependent rate coefficients

The pressure-dependent rate coefficients of the bimolecular reactions were computed in two ways – by the SS-QRRK[1,2,1] method and by the master equation (ME/RRKM)[2-3] method.

For the SS-QRRK calculations, F_E is computed based on the numerically integrated Whitten-Rabinovitch approximation.[4] The collision efficiency is computed based on the exponential-down model[5] (also called the Gilbert-Luther-Troe model[6]) with the energy-transfer-down parameter equal to 300 cm^{-1}. This model also requires Lennard-Jones (L-J) parameters, and the values we used are given in Table S4.

RRKM calculations require microcanonical rate coefficients, and these were obtained by Rice-Ramsperger-Kassel-Marcus (RRKM) theory[7] with parameters obtained by CCSD(T)-F12a/cc-pVTZ-F12//M062X/MG3S for the HO_2 + $C_5H_{11}CHO$/ C_4H_9CHO/ C_3H_7CHO reactions.

Table S1. Electronic structure methods and basis sets

Abbreviation	Explanation	Reference
CCSD(T)	Coupled cluster theory with single and double excitations and quasiperturbative connected triples	[8]
CCSD(T)-F12a	CCSD(T) with explicit correlation of type F12a	[9,10]
M06-2X	M06-2X hybrid meta GGA density functional	[11]
M11-L	M11-L local meta generalized gradient approximation density functional	[12]
MN15-L	MN15-L local meta nonseparable gradient approximation density functional	[13]
A/B[a]	A calculation with electronic structure approximation A and basis set B	
A/B//C/D[b,c]	A single-point energy calculation with method A/B at a geometry optimized by method C/D and with frequencies by method C/D.	
cc-pVTZ-F12	A polarized valence-triple-zeta basis set for explicitly correlated calculations	[14]
cc-pVDZ-F12	A polarized valence-double-zeta basis set for explicitly correlated calculations	[15]
MG3S	A minimally augmented polarized valence-triple-zeta basis set	[16]
A/B//C/D[b,c]	A single-point energy calculation with method A/B at a geometry optimized by method C/D and with frequencies by method C/D.	
CC/TZ-F12//	abbreviation used in this article for CCSD(T)-F2a/cc-pVTZ-F12//M06-2X/MG3S	
CC/DZ-F12//	abbreviation used in this article for CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S	

Table S2. Standard scale factors applied to vibrational frequencies [a]

Methods	Scale Factor
M06-2X/MG3S	0.970
M11-L /MG3S	0.985
MN15-L/MG3S	0.977

[a] The scale factors are calculated by the method in Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G., Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries. *J. Chem. Theory Comput.* 2010, *6*, 2872-2887.

Table S3. Specific-reaction-parameter scale factors calculated by using the MPW1K/MG3S method for the HO_2 + $C_5H_{11}CHO$, HO_2 + C_4H_9CHO, HO_2 + C_3H_7CHO, and H-shift reactions [a,b]

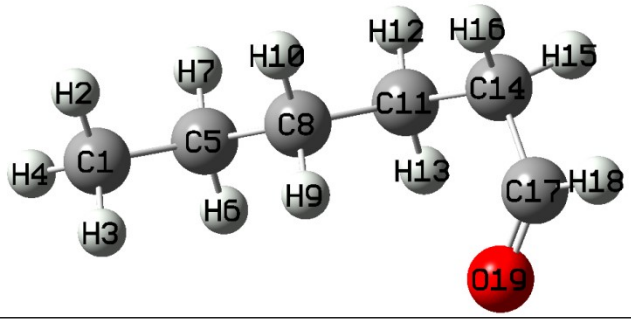
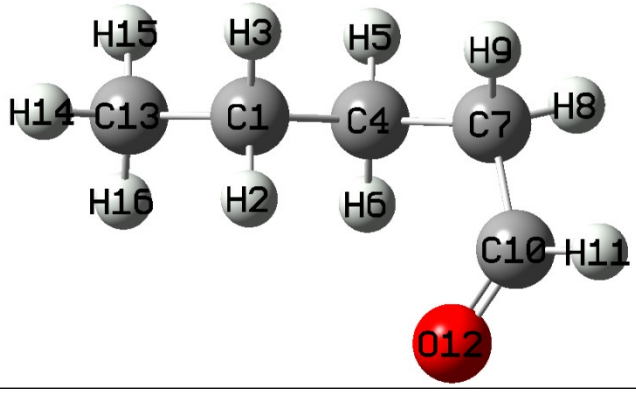
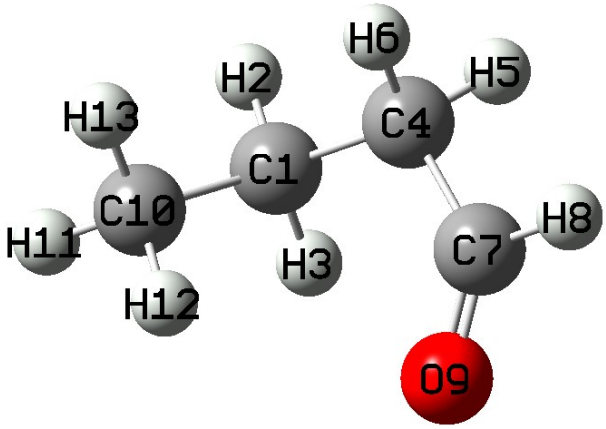
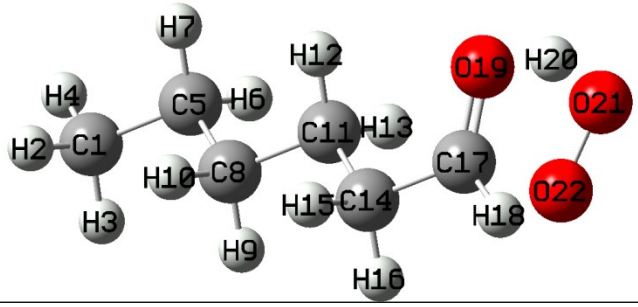
	$C_6H_{12}O$	$C_5H_{10}O$	C_4H_8O	HO_2	TS1A	TS1B	TS1C
λ^{Anh}	0.987[c]	0.987[c]	0.987[c]	0.985	0.984	0.983	0.982
λ^{ZPE}	0.970[c]	0.970[c]	0.970[c]	0.967	0.967	0.966	0.965
	M1A	M1B	M1C	TS2A	TS2B	TS2C	C1A, C1B, C1C
λ^{Anh}	0.986[c]	0.987[c]	0.987[c]	0.986	0.985	0.985	0.986[c]
λ^{ZPE}	0.970[c]	0.970[c]	0.970[c]	0.968	0.967	0.967	0.970[c]

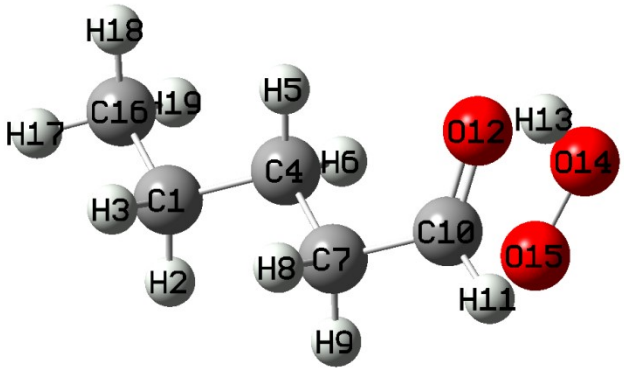
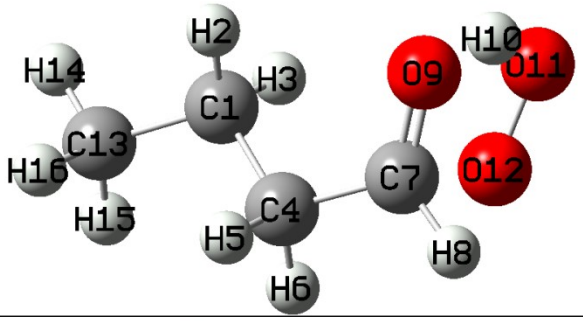
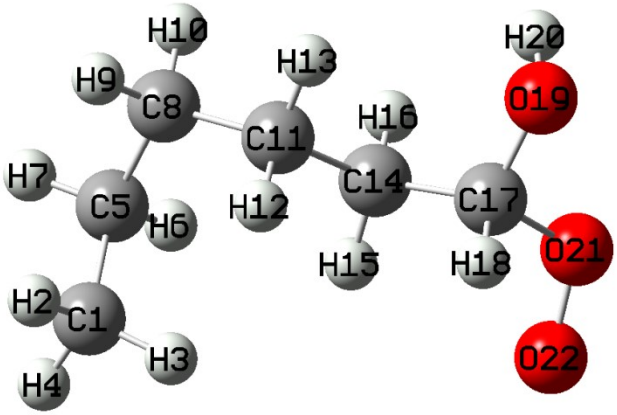
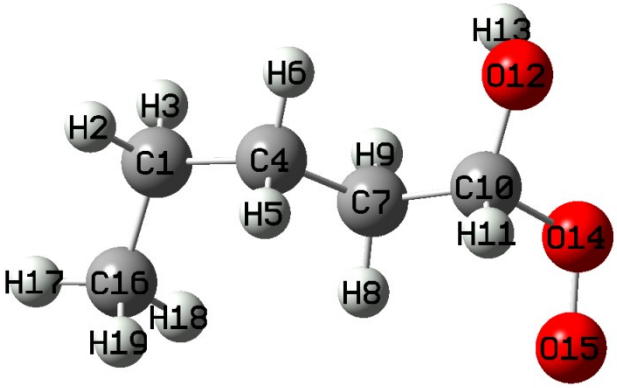
[a] λ^{Anh} equals the ratio of anharmonic zero-point vibrational energy to harmonic zero-point vibrational energy of the MPW1K/MG3S method.

[b] λ^{ZPE} equals the product of λ^{Anh} and the generic parameter λ^{H}, where λ^{H} is obtained from previous studies that gave λ^{H} equal to 0.982 for M06-2X/MG3S.

[c] For the aldehydes, the adducts, and the products of the H-shift reactions, we use the standard scale factors.

Table S4. Numbers of distinguishable structures and torsions

		distinguishable structures	torsions
$C_5H_{11}CHO$		27	2-1-5-8 1-5-8-11 5-8-11-14 8-11-14-17 11-14-17-19
C_4H_9CHO		9	14-13-1-4 13-1-4-7 1-4-7-10 4-7-10-12
C_3H_7CHO		3	11-10-1-4 10-1-4-7 1-4-7-9
TS1A		33	2-1-5-8 1-5-8-11 5-8-11-14 8-11-14-17 11-14-17-18

TS1B		16	17-16-1-4 16-1-4-7 1-4-7-10 4-7-10-11
TS1C		9	15-13-1-4 13-1-4-7 1-4-7-8
M1A		256	2-1-5-8 1-5-8-11 5-8-11-14 8-11-14-17 11-14-17-21 14-17-21-22 18-17-19-20
M1B		30	17-16-1-4 16-1-4-7 1-4-7-10 4-7-10-14 7-10-14-15 11-10-12-13

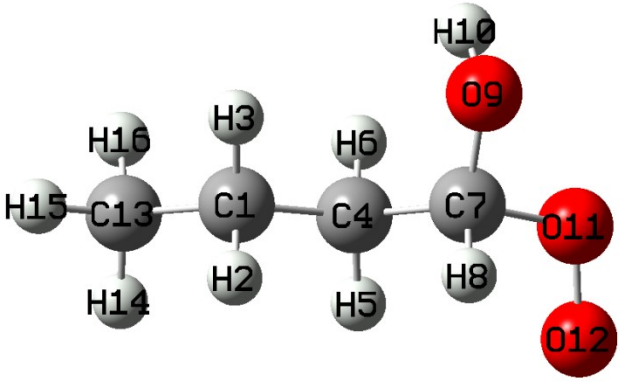
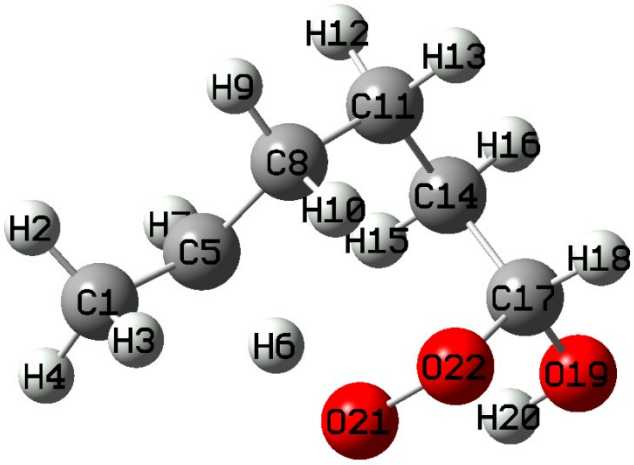
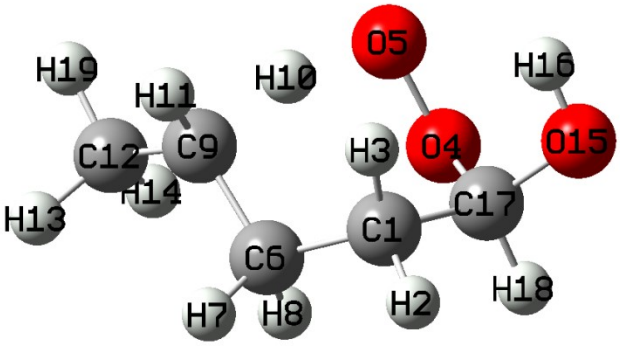
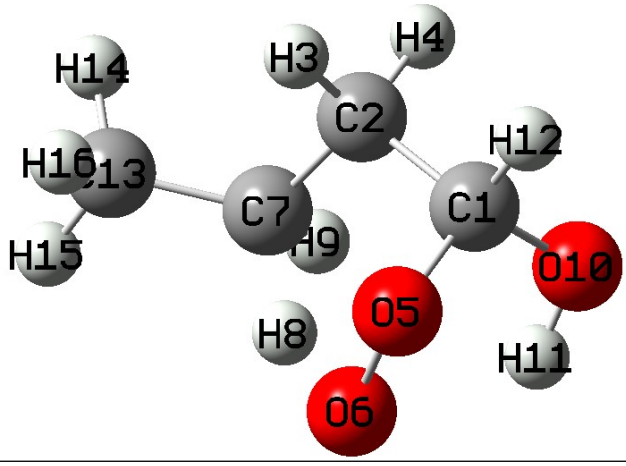
M1C		31	15-13-1-4 13-1-4-7 1-4-7-11 4-7-11-12 8-7-9-10
TS2A		2	2-1-5-8 14-17-19-20
TS2B		2	13-12-9-6 1-17-15-16
TS2C		2	14-13-7-2 2-1-10-11

Table S5. Lennard-Jones parameters for calculations of collision rates used in the pressure-dependent calculations

Molecule	ε (in K)	σ (in Å)	Reference
N_2	82	3.74	17
He	10	2.55	23
HO_2	289.3	4.20	18
C_4H_8O	148.02	4.35	19
$C_5H_{10}O$	171.37	4.34	25
$C_6H_{12}O$	178.29	4.70	25

Table S6. Barrier heights, enthalpies of activation at 0 K (in kcal/mol), and their mean unsigned deviations from the reference values for the HO_2 reactions with $C_5H_{11}CHO$, C_4H_9CHO, and C_3H_7CHO (reactions R1–R2) as calculated using various theoretical methods with the standard vibrational scale factors

Method	TS1A[a]		
	$\Delta V^{\ddagger}$	$\Delta H_0^{\ddagger}$	MUD[b]
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S	-2.28	-1.67	0.00[c]
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S	-2.21	-1.60	0.07
M11-L /MG3S	-1.38	-1.11	0.73
M06-2X/MG3S	-3.92	-3.31	1.64
Method	TS1B[d]		
	$\Delta V^{\ddagger}$	$\Delta H_0^{\ddagger}$	MUD[b]
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S	-2.29	-1.68	0.00[c]
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S	-2.22	-1.61	0.07
M11-L/MG3S	-1.35	-1.04	0.79
M06-2X/MG3S	-3.90	-3.29	1.61
Method	TS1C[e]		
	$\Delta V^{\ddagger}$	$\Delta H_0^{\ddagger}$	MUD[b]
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S	-2.33	-1.69	0.00[c]
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S	-2.56	-1.61	0.07
M11-L/MG3S	-1.38	-1.04	0.80
M06-2X/MG3S	-3.94	-3.29	1.60

[a]TS1A is the lowest-energy transition structure of the HO_2 + $C_5H_{11}CHO$ reaction (R1).

[b]MUD is mean unsigned deviation with respect to the first row. The mean unsigned deviation (MUD) is the average of the absolute error of the values in the previous two columns.

[c]These values are zero by definition since this is the reference value.

[d]TS1B is the lowest-energy transition structure of the HO_2 + C_4H_9CHO reaction (R2).

[e]TS1C is the lowest-energy transition structure of the HO_2 + C_3H_7CHO reaction (R3).

Table S7. The relative enthalpies at 0 K (in kcal/mol), and their mean unsigned deviations from the reference values for the H-shift reactions (reactions R4–R6) as calculated using various theoretical methods with the standard vibrational scale factors

Method	ΔH_0		
	TS2A[a]	M2A	MUD[b]
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S	17.13	9.05	0.00
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S	17.91	9.83	0.78
MN15-L/MG3S	15.62	8.58	0.99
M11-L/MG3S	14.78	6.65	2.37

Method	ΔH_0		
	$TS2B$[c]	M2B	MUD[b]
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S	19.26	9.14	0.00
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S	19.43	9.31	0.17
MN15-L/MG3S	16.87	7.59	1.97
M11-L/MG3S	16.14	6.21	3.02

Method	ΔH_0		
	TS2C[d]	M2C	MUD[b]
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S	21.45	9.47	0.00
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S	21.63	9.65	0.18
MN15-L/MG3S	19.42	7.35	2.07
M11-L/MG3S	18.16	6.76	3.00

[a]TS2A is the lowest-energy transition structure of 1, 7-H-shift reaction (R4) of M1A.

[b]MUD is mean unsigned deviation with respect to the first row. The mean unsigned deviation (MUD) is the average of the absolute error of the values in the previous two columns.

[c]TS2B is the lowest-energy transition structure for the 1, 6-H-shift reaction (R5) of M1B.

[d]TS2C is the lowest-energy transition structure for the 1, 5-H-shift reaction (R6) of M1C.

Table S8. Tunneling and recrossing transmission coefficients, torsional anharmonic factors, high-pressure-limit (HPL) rate coefficients (cm^3 $molecule^{-1}$ s^{-1}), and HPL activation energies (kcal/mol) for the HO_2 + $C_5H_{11}CHO$ reaction (reaction R1 with lowest-energy transition structure TS1A and other conformers included by the multistructural torsional anharmonicity factor)

$T(K)$	F_{fwd}^{MS-T} [a]	k_{SS-TST}^{HL} [b]	Γ_{SS-CVT}^{LL} [c]	k_{SS-SCT}^{LL} [d]	k_{R1} [e]	E_{af}
190	1.15	3.16E-13	3.71E-01	4.73	6.40E-13	-2.96
200	1.15	2.36E-13	3.92E-01	4.06	4.33E-13	-2.91
210	1.15	1.82E-13	4.11E-01	3.56	3.07E-13	-2.85
220	1.15	1.43E-13	4.30E-01	3.18	2.26E-13	-2.79
230	1.15	1.15E-13	4.47E-01	2.89	1.72E-13	-2.73
240	1.15	9.49E-14	4.64E-01	2.65	1.34E-13	-2.68
250	1.15	7.93E-14	4.79E-01	2.45	1.08E-13	-2.63
260	1.15	6.73E-14	4.94E-01	2.29	8.80E-14	-2.57
270	1.16	5.78E-14	5.07E-01	2.16	7.33E-14	-2.52
280	1.16	5.03E-14	5.20E-01	2.05	6.20E-14	-2.47
290	1.16	4.43E-14	5.33E-01	1.95	5.33E-14	-2.42
298	1.16	4.02E-14	5.42E-01	1.89	4.75E-14	-2.38
300	1.16	3.93E-14	5.44E-01	1.87	4.63E-14	-2.37
310	1.16	3.53E-14	5.55E-01	1.80	4.08E-14	-2.32
320	1.16	3.19E-14	5.65E-01	1.73	3.62E-14	-2.27
330	1.16	2.90E-14	5.75E-01	1.68	3.25E-14	-2.23
340	1.16	2.66E-14	5.84E-01	1.63	2.94E-14	-2.18
350	1.16	2.45E-14	5.92E-01	1.59	2.68E-14	-2.13

[a] F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor calculated with the standard scale factor.

[b] k_{SS-TST}^{HL} is the HL level calculation by conventional transition state theory without a transmission coefficient with the specific-reaction-parameter scale factor.

[c] Γ_{SS-CVT}^{LL} is the LL recrossing transmission coefficient, which equals $k_{SS-CVT}^{LL}/k_{SS-TST}^{LL}$ calculated with the standard scale factor.

[d] k_{SS-SCT}^{LL} is the LL tunneling transmission coefficient calculated by the small-curvature tunneling approximation with the standard scale factor.

[e] The high-pressure-limit rate coefficient given by eq S1. HL is CCSD(T)-F12a/cc-pVTZ//M06-2X/MG3S, and LL is M11-L/MG3S. This bimolecular reaction is considered to be independent of pressure, and so the high-pressure limit (HPL) applies at all pressures.

[f] E_a is Arrhenius activation energy (kcal/mol) for the high-pressure limit, which is calculated as $-R\dfrac{d\ln k_{1b}}{d(1/T)}$.

Table S9. Tunneling and recrossing transmission coefficients, torsional anharmonic factors, high-pressure-limit (HPL) rate coefficients (cm^3 $molecule^{-1}$ s^{-1}), and HPL activation energies (kcal/mol) for the HO_2 + C_4H_9CHO reaction (reaction R2 with lowest-energy transition structure TS1B and other conformers included by the multistructural torsional anharmonicity factor)

$T(K)$	F_{fwd}^{MS-T} [a]	k_{SS-TST}^{HL} [b]	Γ_{SS-CVT}^{LL} [c]	k_{SS-SCT}^{LL} [d]	k_{R2} [e]	E_a [f]
190	1.91	3.75E-13	3.60E-01	4.87	1.26E-12	-2.99
200	1.93	2.78E-13	3.81E-01	4.15	8.48E-13	-2.93
210	1.94	2.12E-13	4.00E-01	3.63	5.99E-13	-2.88
220	1.95	1.66E-13	4.19E-01	3.23	4.39E-13	-2.83
230	1.96	1.33E-13	4.36E-01	2.92	3.33E-13	-2.78
240	1.96	1.09E-13	4.52E-01	2.68	2.59E-13	-2.73
250	1.97	9.05E-14	4.68E-01	2.48	2.07E-13	-2.68
260	1.97	7.64E-14	4.83E-01	2.31	1.68E-13	-2.63
270	1.97	6.54E-14	4.96E-01	2.18	1.40E-13	-2.58
280	1.97	5.67E-14	5.10E-01	2.06	1.18E-13	-2.54
290	1.97	4.97E-14	5.22E-01	1.96	1.00E-13	-2.49
298	1.97	4.50E-14	5.31E-01	1.89	8.93E-14	-2.46
300	1.97	4.40E-14	5.34E-01	1.88	8.70E-14	-2.45
310	1.97	3.93E-14	5.45E-01	1.80	7.61E-14	-2.40
320	1.97	3.54E-14	5.55E-01	1.74	6.73E-14	-2.36
330	1.97	3.22E-14	5.65E-01	1.68	6.01E-14	-2.32
340	1.96	2.94E-14	5.74E-01	1.63	5.41E-14	-2.27
350	1.96	2.71E-14	5.83E-01	1.59	4.91E-14	-2.23

[a] F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor calculated with the standard scale factor.

[b] k_{SS-TST}^{HL} is the HL level calculation by conventional transition state theory without a transmission coefficient with the specific-reaction-parameter scale factor.

[c] Γ_{SS-CVT}^{LL} is the LL recrossing transmission coefficient, which equals $k_{SS-CVT}^{LL}/k_{SS-TST}^{LL}$ calculated with the standard scale factor.

[d] k_{SS-SCT}^{LL} is the LL tunneling transmission coefficient calculated by the small-curvature tunneling approximation with the standard scale factor.

[e] The high-pressure-limit rate coefficient given by eq S1. HL is CCSD(T)-F12a/cc-pVTZ//M06-2X/MG3S, and LL is M11-L/MG3S. This bimolecular reaction is considered to be independent of pressure, and so the high-pressure limit (HPL) applies at all pressures.

[f] E_a is the Arrhenius activation energy (kcal/mol) for the high-pressure limit, which is calculated as $-R\dfrac{d\ln k_{2b}}{d(1/T)}$.

Table S10. Tunneling and recrossing transmission coefficients, torsional anharmonic factors, high-pressure-limit (HPL) rate coefficients (cm^3 $molecule^{-1}$ s^{-1}), and HPL activation energies (kcal/mol) for the $HO_2 + C_4H_9CHO$ reaction (reaction R3 with lowest-energy transition structure TS1C and other conformers included by the multistructural torsional anharmonicity factor)

$T(K)$	F_{fwd}^{MS-T} [a]	k_{SS-TST}^{HL} [b]	Γ_{SS-CVT}^{LL} [c]	k_{SS-SCT}^{LL} [d]	k_{R3} [e]	E_a [f]
190	1.39	4.21E-13	3.45E-01	4.75	9.58E-13	-3.06
200	1.39	3.11E-13	3.65E-01	4.06	6.40E-13	-3.00
210	1.39	2.36E-13	3.84E-01	3.56	4.49E-13	-2.94
220	1.39	1.84E-13	4.02E-01	3.17	3.27E-13	-2.88
230	1.39	1.47E-13	4.18E-01	2.87	2.46E-13	-2.83
240	1.40	1.20E-13	4.34E-01	2.63	1.91E-13	-2.77
250	1.40	9.93E-14	4.49E-01	2.44	1.52E-13	-2.71
260	1.40	8.36E-14	4.64E-01	2.28	1.23E-13	-2.66
270	1.40	7.14E-14	4.77E-01	2.15	1.02E-13	-2.61
280	1.40	6.17E-14	4.90E-01	2.03	8.60E-14	-2.55
290	1.40	5.40E-14	5.02E-01	1.94	7.35E-14	-2.50
298	1.40	4.88E-14	5.11E-01	1.87	6.53E-14	-2.46
300	1.40	4.77E-14	5.13E-01	1.85	6.36E-14	-2.45
310	1.40	4.25E-14	5.24E-01	1.78	5.56E-14	-2.40
320	1.40	3.82E-14	5.34E-01	1.72	4.92E-14	-2.35
330	1.40	3.47E-14	5.43E-01	1.67	4.40E-14	-2.30
340	1.40	3.16E-14	5.52E-01	1.62	3.96E-14	-2.25
350	1.40	2.91E-14	5.61E-01	1.57	3.60E-14	-2.20

[a] F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor calculated with the standard scale factor.

[b] k_{SS-TST}^{HL} is the HL level calculation by conventional transition state theory without a transmission coefficient with the specific-reaction-parameter scale factor.

[c] Γ_{SS-CVT}^{LL} is the LL recrossing transmission coefficient, which equals $k_{SS-CVT}^{LL}/k_{SS-TST}^{LL}$ calculated with the standard scale factor.

[d] k_{SS-SCT}^{LL} is the LL tunneling transmission coefficient calculated by the small-curvature tunneling approximation with the standard scale factor.

[e] The high-pressure-limit rate coefficient given by eq S1. HL is CCSD(T)-F12a/cc-pVTZ//M06-2X/MG3S, and LL is M11-L/MG3S.

[f] E_a is Arrhenius activation energy (kcal/mol) for the high-pressure limit, which is calculated as $-R\dfrac{d\ln k_{3b}}{d(1/T)}$.

Table S11. Tunneling and recrossing transmission coefficients, torsional anharmonic factors, high-pressure-limit (HPL) rate coefficients (s^{-1}), and HPL activation energies (kcal/mol) for reaction R4

$T(K)$	F_{fwd}^{MS-T} [a]	k_{SS-TST}^{HL} [b]	Γ_{SS-CVT}^{LL} [c]	k_{SS-SCT}^{LL} [d]	k_{1u} [e]	E_a [f]
190	0.37	1.24E-08	9.33E-01	556.56	2.39E-06	12.98
200	0.34	1.15E-07	9.34E-01	336.35	1.24E-05	12.79
210	0.32	8.59E-07	9.35E-01	216.54	5.57E-05	12.66
220	0.30	5.35E-06	9.35E-01	146.87	2.19E-04	12.57
230	0.28	2.84E-05	9.36E-01	104.04	7.70E-04	12.52
240	0.26	1.31E-04	9.36E-01	76.47	2.44E-03	12.50
250	0.24	5.37E-04	9.36E-01	57.98	7.10E-03	12.51
260	0.23	1.97E-03	9.36E-01	45.17	1.90E-02	12.55
270	0.21	6.58E-03	9.37E-01	36.01	4.75E-02	12.61
280	0.20	2.02E-02	9.37E-01	29.30	1.11E-01	12.69
290	0.19	5.72E-02	9.37E-01	24.27	2.46E-01	12.78
298	0.18	1.25E-01	9.37E-01	21.11	4.47E-01	12.87
300	0.18	1.51E-01	9.37E-01	20.41	5.17E-01	12.90
310	0.17	3.76E-01	9.37E-01	17.42	1.04E+00	13.03
320	0.16	8.85E-01	9.37E-01	15.04	1.99E+00	13.17
330	0.15	1.98E+00	9.37E-01	13.14	3.68E+00	13.32
340	0.14	4.21E+00	9.37E-01	11.59	6.56E+00	13.49
350	0.14	8.60E+00	9.37E-01	10.32	1.13E+01	13.67

[a] F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor calculated with the standard scale factor.

[b] k_{SS-TST}^{HL} is the HL level calculation by conventional transition state theory without a transmission coefficient with the specific-reaction-parameter scale factor.

[c] Γ_{SS-CVT}^{LL} is the LL recrossing transmission coefficient, which equals $k_{SS-CVT}^{LL}/k_{SS-TST}^{LL}$ calculated with the standard scale factor.

[d] k_{SS-SCT}^{LL} is the LL tunneling transmission coefficient calculated by the small-curvature tunneling approximation with the standard scale factor.

[e] The high-pressure-limit rate coefficient given by eq S1. HL is CCSD(T)-F12a/cc-pVTZ//M06-2X/MG3S, and LL is MM15-L/MG3S.

[f] E_a is Arrhenius activation energy (kcal/mol) for the high-pressure limit, which is calculated as $-R\dfrac{d\ln k_{1u}}{d(1/T)}$.

Table S12. The tunneling and recrossing transmission coefficients, the torsional anharmonic factors, high-pressure-limit (HPL) rate coefficients (s^{-1}), and HPL activation energies (kcal/mol) for the M1B isomerism reaction (reaction R5 with lowest-energy transition structure TS2B)

$T(K)$	F_{fwd}^{MS-T} [a]	k_{SS-TST}^{HL} [b]	Γ_{SS-CVT}^{LL} [c]	k_{SS-SCT}^{LL} [d]	k_{2u} [e]	E_a [f]
190	0.40	6.81E-11	8.01E-01	769.34	1.69E-08	14.63
200	0.38	8.43E-10	8.06E-01	421.96	1.08E-07	14.49
210	0.35	8.21E-09	8.10E-01	251.74	5.95E-07	14.42
220	0.33	6.50E-08	8.14E-01	160.70	2.85E-06	14.39
230	0.32	4.30E-07	8.17E-01	108.41	1.20E-05	14.40
240	0.30	2.43E-06	8.20E-01	76.58	4.57E-05	14.45
250	0.28	1.20E-05	8.22E-01	56.22	1.57E-04	14.53
260	0.27	5.21E-05	8.25E-01	42.64	4.96E-04	14.63
270	0.26	2.03E-04	8.27E-01	33.27	1.44E-03	14.76
280	0.25	7.21E-04	8.29E-01	26.59	3.91E-03	14.90
290	0.24	2.34E-03	8.30E-01	21.70	9.96E-03	15.06
298	0.23	5.68E-03	8.31E-01	18.69	2.01E-02	15.20
300	0.23	7.04E-03	8.32E-01	18.04	2.39E-02	15.24
310	0.22	1.97E-02	8.33E-01	15.24	5.43E-02	15.43
320	0.21	5.18E-02	8.34E-01	13.06	1.18E-01	15.63
330	0.20	1.28E-01	8.35E-01	11.34	2.44E-01	15.85
340	0.19	3.02E-01	8.36E-01	9.95	4.87E-01	16.07
350	0.19	6.76E-01	8.36E-01	8.83	9.35E-01	16.30

[a] F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor calculated with the standard scale factor.

[b] k_{SS-TST}^{HL} is the HL level calculation by conventional transition state theory without a transmission coefficient with the specific-reaction-parameter scale factor.

[c] Γ_{SS-CVT}^{LL} is the LL recrossing transmission coefficient, which equals $k_{SS-CVT}^{LL}/k_{SS-TST}^{LL}$ calculated with the standard scale factor.

[d] k_{SS-SCT}^{LL} is the LL tunneling transmission coefficient calculated by the small-curvature tunneling approximation with the standard scale factor.

[e] The high-pressure-limit rate coefficient given by eq S1. HL is CCSD(T)-F12a/cc-pVTZ//M06-2X/MG3S, and LL is MN15-L/MG3S.

[f] E_a is Arrhenius activation energy (kcal/mol) for the high-pressure limit, which is calculated as $-R\dfrac{d\ln k_{2u}}{d(1/T)}$.

Table S13. The tunneling and recrossing transmission coefficients, the torsional anharmonic factors, high-pressure-limit (HPL) rate coefficients (s^{-1}), and HPL activation energies (kcal/mol) for the M1C isomerism reaction (reaction R6 with lowest-energy transition structure TS2C)

$T(K)$	F_{fwd}^{MS-T} [a]	k_{SS-TST}^{HL} [b]	Γ_{SS-CVT}^{LL} [c]	k_{SS-SCT}^{LL} [d]	k_{3u} [e]	E_{a6} [f]
190	0.41	4.63E-13	8.16E-01	355060.00	5.51E-08	9.33
200	0.39	7.70E-12	8.20E-01	81840.00	2.04E-07	9.56
210	0.38	9.80E-11	8.24E-01	21963.00	6.73E-07	9.86
220	0.37	9.90E-10	8.27E-01	6755.10	2.02E-06	10.23
230	0.35	8.18E-09	8.30E-01	2356.00	5.62E-06	10.65
240	0.34	5.67E-08	8.32E-01	925.82	1.48E-05	11.13
250	0.33	3.37E-07	8.34E-01	408.48	3.75E-05	11.65
260	0.32	1.74E-06	8.36E-01	201.72	9.30E-05	12.21
270	0.31	7.99E-06	8.38E-01	110.92	2.27E-04	12.81
280	0.30	3.29E-05	8.40E-01	67.30	5.50E-04	13.44
290	0.29	1.23E-04	8.41E-01	44.48	1.32E-03	14.09
298	0.28	3.31E-04	8.42E-01	33.63	2.62E-03	14.63
300	0.28	4.20E-04	8.42E-01	31.56	3.11E-03	14.77
310	0.27	1.33E-03	8.43E-01	23.70	7.16E-03	15.47
320	0.26	3.91E-03	8.44E-01	18.60	1.61E-02	16.19
330	0.25	1.08E-02	8.45E-01	15.12	3.51E-02	16.94
340	0.25	2.81E-02	8.46E-01	12.63	7.43E-02	17.69
350	0.24	6.91E-02	8.47E-01	10.78	1.52E-01	18.47

[a] F_{fwd}^{MS-T} is the multistructural torsional anharmonicity factor calculated with the standard scale factor.

[b] k_{SS-TST}^{HL} is the HL level calculation by conventional transition state theory without a transmission coefficient with the specific-reaction-parameter scale factor.

[c] Γ_{SS-CVT}^{LL} is the LL recrossing transmission coefficient, which equals $k_{SS-CVT}^{LL}/k_{SS-TST}^{LL}$ calculated with the standard scale factor.

[d] k_{SS-SCT}^{LL} is the LL tunneling transmission coefficient calculated by the small-curvature tunneling approximation with the standard scale factor.

[e] The high-pressure-limit rate coefficient given by eq S1. HL is CCSD(T)-F12a/cc-pVTZ//M06-2X/MG3S, and LL is MN15-L/MG3S.

[f] E_a is Arrhenius activation energy (kcal/mol) for the high-pressure limit, which is calculated as $-R\dfrac{d\ln k_{3u}}{d(1/T)}$.

Table S14. Fitting parameters for the high-pressure-limit (HPL) rate coefficients[a]

Rate coefficient	Reaction	ln A	n	E	T_0
k_{R1}	R1	-36.38	1.98	-3.13	18.74
k_{R2}	R2	-35.64	1.74	-3.08	18.80
k_{R3}	R3	-36.25	2.04	-3.23	18.77
k_{1u}	R4	-1.72	17.29	-6.55	-89.02
k_{2u}	R5	-1.86	19.04	-4.78	-92.25
k_{3u}	R6	-39.25	50.73	-27.90	-37.69

[a] A is in cc molecule^{-1} s^{-1}; n is unitless; E is in kcal/mol; and T_0 is in K.

Table S15. The conventional transition state theory (TST) rate coefficients (10^{-14} cm^3 molecule^{-1} s^{-1}) without a transmission coefficient for the HO_2 + RCHO (R = C_5H_{11} C_4H_9, and C_3H_7) reactions and the resulting multistructural torsional anharmonicity factors[a,b,c]

	R1		R2		R3		R1	R2	R3
$T(K)$	k_{SS-TST}^{HL}	k_{SS-TST}^{HLS}	k_{SS-TST}^{HL}	k_{SS-TST}^{HLS}	k_{SS-TST}^{HL}	k_{SS-TST}^{HLS}	F_{fwd}^{MS-T}	F_{fwd}^{MS-T}	F_{fwd}^{MS-T}
190	31.6	14.1	37.5	14.7	42.1	16.1	2.24	2.55	2.61
200	23.6	11.0	27.8	11.5	31.1	12.5	2.15	2.43	2.48
210	18.2	8.78	21.2	91.6	23.6	9.96	2.07	2.32	2.37
220	14.3	7.17	16.6	7.46	18.4	8.10	2.00	2.23	2.28
230	11.5	5.97	13.3	6.20	14.7	6.71	1.94	2.15	2.19
240	9.49	5.05	10.9	5.24	1.20	5.66	1.88	2.08	2.12
250	7.93	4.33	9.05	4.49	9.93	4.84	1.83	2.02	2.05
260	6.73	3.77	7.64	3.90	8.36	4.19	1.78	1.96	1.99
270	5.78	3.32	6.54	3.43	7.14	3.68	1.74	1.91	1.94
280	5.03	2.95	5.67	3.05	6.17	3.26	1.71	1.86	1.89
290	4.43	2.65	4.97	2.73	5.40	2.92	1.67	1.82	1.85
298	4.02	2.44	4.50	2.52	4.88	2.69	1.64	1.79	1.81
300	3.93	2.40	4.40	2.47	4.77	2.64	1.64	1.78	1.81
310	3.53	2.19	3.93	2.25	4.25	2.40	1.61	1.75	1.77
320	3.19	2.01	3.54	2.07	3.82	2.20	1.59	1.71	1.74
330	2.90	1.86	3.22	1.91	3.47	2.03	1.56	1.68	1.71
340	2.66	1.73	2.94	1.78	3.16	1.89	1.54	1.65	1.68
350	2.45	1.62	2.71	1.66	2.91	1.76	1.52	1.63	1.65

[a] k_{SS-TST}^{HL} is the conventional transition state theory rate coefficient calculated using the specific reaction parameter scale factor.

[b] k_{SS-TST}^{HLS} is the conventional transition state theory rate coefficients calculated using the standard scale factor.

[c] F_{fwd}^{MS-T} is $k_{SS-TST}^{HL}/k_{SS-TST}^{HLS}$

Table S16. The conventional transition state theory (TST) rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) without a transmission coefficient for reactions R4–R6 and the resulting multistructural torsional anharmonicity factors[a,b,c]

	R4	R4	R5	R5	R6	R6	R4	R5	R6
$T(K)$	k_{SS-TST}^{HL}	k_{SS-TST}^{HLS}	k_{SS-TST}^{HL}	k_{SS-TST}^{HLS}	k_{SS-TST}^{HL}	k_{SS-TST}^{HLS}	F_{fwd}^{MS-T}	F_{fwd}^{MS-T}	F_{fwd}^{MS-T}
190	1.24E-8	6.64E-9	6.81E-11	4.01E-11	4.63E-13	2.41E-13	1.87	1.70	1.92
200	1.15E-7	6.32E-8	8.43E-10	5.09E-10	7.70E-12	4.15E-12	1.82	1.66	1.86
210	8.59E-7	4.86E-7	8.21E-9	5.07E-9	9.80E-11	5.43E-11	1.77	1.62	1.81
220	5.35E-6	3.10E-6	6.50E-8	4.10E-8	9.90E-10	5.63E-10	1.73	1.59	1.76
230	2.84E-5	1.68E-5	4.30E-7	2.77E-7	8.18E-9	4.76E-9	1.69	1.56	1.72
240	1.31E-4	7.95E-5	2.43E-6	1.59E-6	5.67E-8	3.37E-8	1.65	1.53	1.68
250	5.37E-4	3.31E-4	1.20E-5	7.95E-6	3.37E-7	2.04E-7	1.62	1.50	1.65
260	1.97E-3	1.24E-3	5.21E-5	3.51E-5	1.74E-6	1.08E-6	1.59	1.48	1.62
270	6.58E-3	4.20E-3	2.03E-4	1.39E-4	7.99E-6	5.02E-6	1.57	1.46	1.59
280	2.02E-2	1.31E-2	7.21E-4	4.99E-4	3.29E-5	2.10E-5	1.54	1.44	1.57
290	5.72E-2	3.75E-2	2.34E-3	1.64E-3	1.23E-4	7.95E-5	1.52	1.43	1.55
298	1.25E-1	8.31E-2	5.68E-3	4.02E-3	3.31E-4	2.16E-4	1.50	1.41	1.53
300	1.51E-1	1.01E-1	7.04E-3	4.99E-3	4.20E-4	2.76E-4	1.50	1.41	1.53
310	3.76E-1	2.53E-1	1.97E-2	1.41E-2	1.33E-3	8.82E-4	1.49	1.40	1.51
320	8.85E-1	6.02E-1	5.18E-2	3.74E-2	3.91E-3	2.63E-3	1.47	1.38	1.49
330	1.98	1.36	1.28E-1	9.36E-2	1.08E-2	7.33E-3	1.45	1.37	1.47
340	4.21	2.93	3.02E-1	2.22E-1	2.81E-2	1.92E-2	1.44	1.36	1.46
350	8.60	6.03	6.76E-1	5.01E-1	6.91E-2	4.79E-2	1.43	1.35	1.44

[a] k_{SS-TST}^{HL} is the conventional transition state theory rate coefficient calculated using the specific reaction parameter scale factor.

[b] k_{SS-TST}^{HLS} is the conventional transition state theory rate coefficients calculated using the standard scale factor.

[c] F_{fwd}^{MS-T} is $k_{SS-TST}^{HL}/k_{SS-TST}^{HLS}$

Table S17. The falloff factor *f*(1 bar) (unitless) calculated by SS-QRRK and by ME/RRKM for reactions R1–R3 as functions of temperature

	R1 $HO_2 + C_5H_{11}CHO$		R2 $HO_2 + C_4H_9CHO$		R3 $HO_2 + C_3H_7CHO$	
$T(K)$	SS-QRRK[b]	ME/RRKM[c]	SS-QRRK[b]	ME/RRKM[c]	SS-QRRK[b]	ME/RRKM[c]
190	1.04	1.02	1.02	1.01	1.02	1.01
230	1.11	1.12	1.04	1.04	1.04	1.04
250	1.17	1.23	1.06	1.08	1.06	1.08
270	1.26	1.40	1.09	1.14	1.09	1.14
298	1.48	1.80	1.16	1.30	1.15	1.27
310	1.63	2.04	1.21	1.40	1.19	1.35
330	1.99	2.59	1.33	1.61	1.29	1.53
350	2.57	3.39	1.51	1.91	1.45	1.78

[a]The falloff effect defined as the ratio of $k_\infty(T)$ to $k(T,p)$.

[b]The SS-QRRK falloff effects are obtained by the system-specific quantum Rice–Ramsperger–Kassel method.

[c]The ME/RRKM falloff effects are obtained by the master equation with Rice–Ramsperger–Kassel–Marcus microcanonical rate constants. Note that Rice–Ramsperger–Kassel–Marcus microcanonical rate constants ae the same as conventional transition state theory rate constants for a unimolecular process.

Table S18A. The pressure-dependent rate coefficient $k(T,p)$ (in cm^3 $molecule^{-1}$ s^{-1}) of HO_2 + $C_5H_{11}CHO$ (reaction R1) reaction as calculated by dual-level DL-MS-CVT/SCT /SS-QRRK[a]

$p(bar)$	350 K	330 K	310 K	298 K
0.0316	7.35E-16	1.44E-15	2.81E-15	4.16E-15
0.1	2.11E-15	3.98E-15	7.38E-15	1.06E-14
0.178	3.41E-15	6.21E-15	1.11E-14	1.55E-14
0.316	5.23E-15	9.13E-15	1.55E-14	2.11E-14
0.562	7.58E-15	1.26E-14	2.04E-14	2.68E-14
1	1.04E-14	1.63E-14	2.51E-14	3.22E-14
1.78	1.34E-14	2.00E-14	2.94E-14	3.68E-14
3.16	1.64E-14	2.34E-14	3.30E-14	4.04E-14
5.62	1.91E-14	2.62E-14	3.57E-14	4.30E-14
10	2.15E-14	2.84E-14	3.76E-14	4.47E-14
31.6	2.46E-14	3.09E-14	3.97E-14	4.65E-14
50	2.53E-14	3.15E-14	4.01E-14	4.69E-14
100	2.60E-14	3.20E-14	4.04E-14	4.72E-14
1000	2.67E-14	3.24E-14	4.08E-14	4.75E-14
$p(bar)$	270 K	250 K	230 K	190 K
0.0316	1.05E-14	2.09E-14	4.36E-14	2.90E-13
0.1	2.44E-14	4.53E-14	8.74E-14	4.61E-13
0.178	3.36E-14	5.96E-14	1.10E-13	5.24E-13
0.316	4.29E-14	7.29E-14	1.30E-13	5.69E-13
0.562	5.14E-14	8.41E-14	1.44E-13	5.98E-13
1	5.83E-14	9.25E-14	1.55E-13	6.15E-13
1.78	6.36E-14	9.83E-14	1.62E-13	6.26E-13
3.16	6.72E-14	1.02E-13	1.66E-13	6.32E-13
5.62	6.96E-14	1.05E-13	1.69E-13	6.35E-13
10	7.11E-14	1.06E-13	1.70E-13	6.37E-13
31.6	7.26E-14	1.07E-13	1.71E-13	6.39E-13
50	7.28E-14	1.08E-13	1.72E-13	6.39E-13
100	7.31E-14	1.08E-13	1.72E-13	6.40E-13
1000	7.33E-14	1.08E-13	1.72E-13	6.40E-13

[a]The specific reaction parameter scale factor and multistructural torsional anharmonicity factor are used. The HPL rate constants in this table agree with those in Table S8.

Table S18B. The temperature–pressure dependent rate coefficient $k(T,p)$ (in cm^3 $molecule^{-1}$ s^{-1}) of HO_2 + $C_5H_{11}CHO$ (reaction R1) reaction as calculated by the ME/RRKM with the higher level of electronic structure[a] (CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S)

$p(bar)$	350 K	330 K	310 K	298 K
0.0316	3.34E-16	6.48E-16	1.29E-15	1.96E-15
0.1	7.66E-16	1.40E-15	2.59E-15	3.77E-15
0.178	1.12E-15	1.98E-15	3.53E-15	5.03E-15
0.316	1.60E-15	2.73E-15	4.68E-15	6.51E-15
0.562	2.23E-15	3.65E-15	6.02E-15	8.16E-15
1	3.01E-15	4.74E-15	7.50E-15	9.90E-15
1.78	3.92E-15	5.94E-15	9.02E-15	1.16E-14
3.16	4.93E-15	7.18E-15	1.05E-14	1.32E-14
5.62	5.99E-15	8.39E-15	1.18E-14	1.46E-14
10	7.00E-15	9.47E-15	1.29E-14	1.56E-14
31.6	8.66E-15	1.11E-14	1.43E-14	1.70E-14
50	9.13E-15	1.15E-14	1.47E-14	1.73E-14
100	9.64E-15	1.19E-14	1.50E-14	1.75E-14
1000	1.02E-14	1.23E-14	1.53E-14	1.78E-14
$p(bar)$	270 K	250 K	230 K	190 K
0.0316	5.47E-15	1.18E-14	2.64E-14	1.64E-13
0.1	9.37E-15	1.84E-14	3.75E-14	1.93E-13
0.178	1.18E-14	2.21E-14	4.28E-14	2.03E-13
0.316	1.43E-14	2.56E-14	4.76E-14	2.11E-13
0.562	1.68E-14	2.89E-14	5.17E-14	2.16E-13
1	1.93E-14	3.18E-14	5.49E-14	2.20E-13
1.78	2.14E-14	3.41E-14	5.73E-14	2.22E-13
3.16	2.31E-14	3.58E-14	5.89E-14	2.23E-13
5.62	2.45E-14	3.71E-14	6.00E-14	2.24E-13
10	2.54E-14	3.79E-14	6.07E-14	2.25E-13
31.6	2.64E-14	3.87E-14	6.14E-14	2.25E-13
50	2.66E-14	3.89E-14	6.15E-14	2.25E-13
100	2.68E-14	3.90E-14	6.16E-14	2.25E-13
1000	2.70E-14	3.91E-14	6.17E-14	2.25E-13

[a]The standard scale factor is used.

Table S19A. The temperature–pressure dependent rate coefficient $k(T,p)$ (in cm^3 $molecule^{-1}$ s^{-1}) of HO_2 + C_4H_9CHO (reaction R2) reaction as calculated by dual-level DL-MS-CVT/SCT /SS-QRRK

$p(bar)$	350 K	330 K	310 K	298 K
0.0316	4.85E-15	8.67E-15	1.53E-14	2.15E-14
0.1	1.15E-14	1.92E-14	3.14E-14	4.19E-14
0.178	1.63E-14	2.59E-14	4.05E-14	5.27E-14
0.316	2.16E-14	3.28E-14	4.92E-14	6.25E-14
0.562	2.72E-14	3.95E-14	5.68E-14	7.07E-14
1	3.25E-14	4.53E-14	6.30E-14	7.70E-14
1.78	3.71E-14	5.00E-14	6.76E-14	8.15E-14
3.16	4.09E-14	5.35E-14	7.08E-14	8.46E-14
5.62	4.38E-14	5.60E-14	7.29E-14	8.65E-14
10	4.58E-14	5.76E-14	7.42E-14	8.77E-14
31.6	4.79E-14	5.93E-14	7.55E-14	8.88E-14
50	4.83E-14	5.96E-14	7.57E-14	8.90E-14
100	4.87E-14	5.98E-14	7.59E-14	8.91E-14
1000	4.91E-14	6.01E-14	7.61E-14	8.93E-14
$p(bar)$	270 K	250 K	230 K	190 K
0.0316	4.77E-14	8.61E-14	1.65E-13	8.86E-13
0.1	8.33E-14	1.40E-13	2.48E-13	1.11E-12
0.178	9.93E-14	1.61E-13	2.78E-13	1.17E-12
0.316	1.12E-13	1.77E-13	2.98E-13	1.21E-12
0.562	1.22E-13	1.88E-13	3.12E-13	1.23E-12
1	1.29E-13	1.96E-13	3.21E-13	1.24E-12
1.78	1.33E-13	2.00E-13	3.26E-13	1.25E-12
3.16	1.36E-13	2.03E-13	3.29E-13	1.25E-12
5.62	1.38E-13	2.05E-13	3.31E-13	1.26E-12
10	1.39E-13	2.06E-13	3.32E-13	1.26E-12
31.6	1.40E-13	2.07E-13	3.33E-13	1.26E-12
50	1.40E-13	2.07E-13	3.33E-13	1.26E-12
100	1.40E-13	2.07E-13	3.33E-13	1.26E-12
1000	1.40E-13	2.07E-13	3.33E-13	1.26E-12

[a]The specific reaction parameter scale factor and multistructural torsional anharmonicity factor are used. The HPL rate constants in this table agree with those in Table S9.

Table S19B. The temperature–pressure dependent rate coefficient $k(T,p)$ (in cm^3 $molecule^{-1}$ s^{-1}) of HO_2 + C_4H_9CHO (reaction R2) reaction as calculated by the ME/RRKM with the higher level of electronic structure[a] (CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S)

$p(bar)$	350 K	330 K	310 K	298 K
0.0316	9.97E-16	1.77E-15	3.18E-15	4.56E-15
0.1	1.99E-15	3.30E-15	5.53E-15	7.56E-15
0.178	2.70E-15	4.33E-15	6.97E-15	9.31E-15
0.316	3.56E-15	5.49E-15	8.50E-15	1.11E-14
0.562	4.54E-15	6.74E-15	1.01E-14	1.28E-14
1	5.59E-15	8.00E-15	1.15E-14	1.44E-14
1.78	6.66E-15	9.20E-15	1.28E-14	1.57E-14
3.16	7.65E-15	1.02E-14	1.38E-14	1.67E-14
5.62	8.52E-15	1.11E-14	1.46E-14	1.74E-14
10	9.23E-15	1.17E-14	1.52E-14	1.79E-14
31.6	1.01E-14	1.25E-14	1.58E-14	1.84E-14
50	1.03E-14	1.26E-14	1.59E-14	1.85E-14
100	1.05E-14	1.28E-14	1.60E-14	1.86E-14
1000	1.07E-14	1.29E-14	1.61E-14	1.87E-14
$p(bar)$	270 K	250 K	230 K	190 K
0.0316	1.09E-14	2.08E-14	4.15E-14	2.12E-13
0.1	1.61E-14	2.83E-14	5.20E-14	2.31E-13
0.178	1.87E-14	3.16E-14	5.61E-14	2.37E-13
0.316	2.11E-14	3.45E-14	5.93E-14	2.41E-13
0.562	2.32E-14	3.67E-14	6.17E-14	2.43E-13
1	2.49E-14	3.84E-14	6.34E-14	2.45E-13
1.78	2.61E-14	3.96E-14	6.45E-14	2.46E-13
3.16	2.70E-14	4.04E-14	6.51E-14	2.46E-13
5.62	2.76E-14	4.09E-14	6.55E-14	2.47E-13
10	2.80E-14	4.12E-14	6.58E-14	2.47E-13
31.6	2.84E-14	4.15E-14	6.60E-14	2.47E-13
50	2.84E-14	4.15E-14	6.60E-14	2.47E-13
100	2.85E-14	4.16E-14	6.61E-14	2.47E-13
1000	2.85E-14	4.16E-14	6.61E-14	2.47E-13

[a]The standard scale factor is used.

Table S20A. The temperature–pressure dependent rate coefficient $k(T,p)$ (in cm^3 $molecule^{-1}$ s^{-1}) of HO_2 + C_3H_7CHO (reaction R3) reaction as calculated by dual-level DL-MS-CVT/SCT /SS-QRRK

$p(bar)$	350 K	330 K	310 K	298 K
0.0316	3.81E-15	6.73E-15	1.14E-14	1.57E-14
0.1	9.10E-15	1.49E-14	2.36E-14	3.11E-14
0.178	1.28E-14	2.01E-14	3.04E-14	3.92E-14
0.316	1.69E-14	2.52E-14	3.68E-14	4.64E-14
0.562	2.10E-14	3.00E-14	4.23E-14	5.23E-14
1	2.48E-14	3.42E-14	4.67E-14	5.68E-14
1.78	2.81E-14	3.74E-14	4.99E-14	6.00E-14
3.16	3.07E-14	3.98E-14	5.21E-14	6.21E-14
5.62	3.26E-14	4.14E-14	5.35E-14	6.34E-14
10	3.39E-14	4.24E-14	5.44E-14	6.42E-14
31.6	3.53E-14	4.35E-14	5.52E-14	6.49E-14
50	3.55E-14	4.37E-14	5.53E-14	6.51E-14
100	3.58E-14	4.38E-14	5.55E-14	6.52E-14
1000	3.60E-14	4.40E-14	5.56E-14	6.53E-14
$p(bar)$	270 K	250 K	230 K	190 K
0.0316	3.35E-14	5.97E-14	1.13E-13	6.17E-13
0.1	5.99E-14	9.99E-14	1.77E-13	8.14E-13
0.178	7.20E-14	1.16E-13	2.01E-13	8.70E-13
0.316	8.16E-14	1.29E-13	2.18E-13	9.06E-13
0.562	8.89E-14	1.38E-13	2.29E-13	9.28E-13
1	9.39E-14	1.43E-13	2.36E-13	9.41E-13
1.78	9.71E-14	1.47E-13	2.40E-13	9.48E-13
3.16	9.91E-14	1.49E-13	2.43E-13	9.53E-13
5.62	1.00E-13	1.50E-13	2.44E-13	9.55E-13
10	1.01E-13	1.51E-13	2.45E-13	9.56E-13
31.6	1.02E-13	1.52E-13	2.46E-13	9.57E-13
50	1.02E-13	1.52E-13	2.46E-13	9.58E-13
100	1.02E-13	1.52E-13	2.46E-13	9.58E-13
1000	1.02E-13	1.52E-13	2.46E-13	9.58E-13

[a]The specific reaction parameter scale factor and multistructural torsional anharmonicity factor are used. The HPL rate constants in this table agree with those in Table S10.

Table S20B. The temperature–pressure dependent rate coefficient $k(T,p)$ (in cm^3 $molecule^{-1}$ s^{-1}) of HO_2 + C_3H_7CHO (reaction R3) reaction as calculated by the ME/RRKM with the higher level of electronic structure[a] (CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S)

$p(bar)$	350 K	330 K	310 K	298K
0.0316	1.27E-15	2.18E-15	3.80E-15	5.35E-15
0.1	2.46E-15	3.96E-15	6.45E-15	8.70E-15
0.178	3.28E-15	5.11E-15	8.04E-15	1.06E-14
0.316	4.24E-15	6.39E-15	9.69E-15	1.25E-14
0.562	5.32E-15	7.74E-15	1.13E-14	1.43E-14
1	6.45E-15	9.07E-15	1.29E-14	1.60E-14
1.78	7.57E-15	1.03E-14	1.42E-14	1.73E-14
3.16	8.58E-15	1.13E-14	1.52E-14	1.83E-14
5.62	9.45E-15	1.22E-14	1.60E-14	1.91E-14
10	1.01E-14	1.28E-14	1.65E-14	1.96E-14
31.6	1.10E-14	1.35E-14	1.71E-14	2.01E-14
50	1.12E-14	1.37E-14	1.72E-14	2.02E-14
100	1.13E-14	1.38E-14	1.73E-14	2.03E-14
1000	1.15E-14	1.39E-14	1.74E-14	2.03E-14
$p(bar)$	270 K	250 K	230 K	190 K
0.0316	1.23E-14	2.32E-14	4.60E-14	2.39E-13
0.1	1.80E-14	3.14E-14	5.76E-14	2.62E-13
0.178	2.08E-14	3.50E-14	6.22E-14	2.70E-13
0.316	2.34E-14	3.81E-14	6.58E-14	2.74E-13
0.562	2.56E-14	4.06E-14	6.85E-14	2.78E-13
1	2.74E-14	4.24E-14	7.04E-14	2.79E-13
1.78	2.87E-14	4.37E-14	7.16E-14	2.81E-13
3.16	2.97E-14	4.46E-14	7.24E-14	2.81E-13
5.62	3.03E-14	4.51E-14	7.28E-14	2.82E-13
10	3.07E-14	4.54E-14	7.31E-14	2.82E-13
31.6	3.11E-14	4.57E-14	7.34E-14	2.82E-13
50	3.11E-14	4.58E-14	7.34E-14	2.82E-13
100	3.12E-14	4.58E-14	7.34E-14	2.82E-13
1000	3.12E-14	4.59E-14	7.35E-14	2.82E-13

[a]The standard scale factor is used from the standard method.

Table S21. NO_3 concentrations (molecules/cc), the rate coefficients (cm^3 $molecule^{-1}$ s^{-1}), and the atmospheric lifetimes (s) with respect to bimolecular reaction as functions of altitude

H^a (km)	T^a (K)	P^a (mbar)	$[NO_3]_a$	$k'_{NO_{3b}}$	$k''_{NO_{3\,b}}$	$k'''_{NO_{3\,b}}$	$\tau'_{NO_{3\,c}}$	$\tau''_{NO_{3\,c}}$	$\tau'''_{NO_{3\,c}}$
0	290.2	1013	3.2×10^{8}	1.91×10^{-14}	1.48×10^{-14}	1.55×10^{-14}	1.64×10^{5}	2.11×10^{5}	2.02×10^{5}
5	250.5	495.9	5.7×10^{6}	5.19×10^{-15}	4.49×10^{-15}	4.03×10^{-15}	3.38×10^{7}	3.91×10^{7}	4.35×10^{7}
10	215.6	242.8	2.5×10^{5}	1.11×10^{-15}	1.09×10^{-15}	8.19×10^{-16}	3.60×10^{9}	3.67×10^{9}	4.88×10^{9}
15	198	118.8	1.5×10^{5}	4.17×10^{-16}	4.42×10^{-16}	2.96×10^{-16}	1.60×10^{10}	1.51×10^{10}	2.25×10^{10}

[a] *H* denotes altitude (atmospheric scale height); *T* denotes temperature; *p* denotes pressure; $[NO_3]$ denotes concentration.[20]

[b] k'_{NO_3}; k''_{NO_3} and k'''_{NO_3} are from the experimental rate coefficients of the NO_3 reactions with RCHO (R = C_5H_{11}, C_4H_9, and C_3H_7). The preferred rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}) of the previous literature.[21]

[c] τ'_{NO_3}; τ''_{NO_3} and τ'''_{NO_3} are the atmosphere lifetimes of OH react with RCHO (R = C_5H_{11}, C_4H_9, and C_3H_7).

Table S22. Volatility estimation of the products from hexanal oxidation.

Pathway	Formula	C*(298 K)[a] (g/m^3)	C*(298 K)[b] (g/m)	Volatility bin
OH oxidation	$C_6H_{12}O_3$	2.29E+06	3.96E+06	IVOC
	$C_6H_{12}O_5$	2.28E+03	1.78E+04	IVOC
	$C_6H_{12}O_4$	1.66E+04	2.91E+04	IVOC
	$C_6H_{10}O_4$	1.62E+05	5.07E+05	IVOC
HO_2 oxidation	$C_6H_{14}O_3$	1.13E+04	2.57E+04	IVOC
	$C_6H_{12}O_4$	7.99E+02	3.28E+03	IVOC
	$C_6H_{14}O_5$	9.94E+00	1.15E+02	SVOC
	$C_6H_{14}O_4$	7.49E+01	1.88E+02	SVOC
	$C_6H_{12}O_4$	2.21E+02	1.33E+03	SVOC

[a]Estimation using EVAPORATION
[b]estimation using SIMPOL1

Table S23. The Cartesian coordinates (Å) of the optimized geometries by M06-2X /MG3S

HO_2	H	-0.87923900	-0.86675500	0.00000000
	O	0.05495200	-0.59862600	0.00000000
	O	0.05495200	0.70697000	0.00000000
C_4H_8O	C	-1.01135400	0.40855500	-0.52911500
	H	-1.73263600	1.19241500	-0.76296000
	H	-0.69610300	-0.03078000	-1.47622100
	C	0.19963900	1.03687500	0.14582500
	H	0.54240500	1.93256700	-0.38394700
	H	-0.03479900	1.37509600	1.16093200
	C	1.39461800	0.12580300	0.23543700
	H	2.25630000	0.52971600	0.80192500
	O	1.46293000	-0.95991900	-0.27029800
	C	-1.67006400	-0.65936300	0.33839400
	H	-2.53510700	-1.09215500	-0.16190300
	H	-0.97058000	-1.46464000	0.55707800
	H	-2.00994900	-0.23408300	1.28423400
$C_5H_{10}O$	C	-1.21829900	-0.06267300	0.50915800
	H	-0.70093600	-0.97807500	0.80005300
	H	-1.34470200	0.53381600	1.41708400
	C	-0.34943700	0.71113300	-0.47842800
	H	-0.85629200	1.63762600	-0.75663200
	H	-0.23231700	0.12394200	-1.39163700
	C	1.02829300	1.03971900	0.07688300
	H	1.55342100	1.77490900	-0.54276800
	H	0.96523000	1.49536600	1.07095200
	C	1.94785300	-0.14781900	0.17960900
	H	2.92637200	0.05180700	0.65832200
	O	1.69163900	-1.24586700	-0.23009100
	C	-2.58297400	-0.40589200	-0.07493200
	H	-3.20003800	-0.94730500	0.64092800
	H	-3.12121600	0.49745700	-0.36619900
	H	-2.47525000	-1.02941000	-0.96311400
$C_6H_{12}O$	C	3.14059400	0.55855800	0.30642400
	H	3.31813000	0.11219100	1.28595500
	H	2.85697800	1.59984800	0.46411400
	H	4.08179500	0.54701600	-0.24194100
	C	2.04494000	-0.19191700	-0.44111800
	H	1.89917500	0.25455700	-1.42780100
	H	2.35632800	-1.22585500	-0.61322600
	C	0.71718600	-0.18411800	0.30708000
	H	0.39720500	0.84870300	0.46310300
	H	0.85988900	-0.62483600	1.29950300
	C	-0.37916000	-0.94721000	-0.42984200
	H	-0.06869400	-1.98512200	-0.56673600
	H	-0.51056700	-0.51820200	-1.42528800
	C	-1.71397200	-0.91557700	0.29969400
	H	-2.42360400	-1.63911000	-0.11653300

	H	-1.60558400	-1.19379000	1.35349800
	C	-2.40806200	0.41944800	0.25169400
	H	-3.33970200	0.48971700	0.84638600
	O	-2.02881200	1.36247300	-0.38557900
C1C	C	-1.98464200	0.27028700	-0.14054800
	H	-2.14086800	-0.14288900	-1.13790100
	H	-2.97120500	0.45273900	0.28671800
	C	-1.26986600	-0.76420900	0.71741100
	H	-0.99007200	-0.35701600	1.69433300
	H	-1.91065900	-1.62697700	0.93319600
	C	-0.02160400	-1.32327800	0.10913600
	H	0.56838400	-1.99168800	0.75900800
	O	0.33940800	-1.11519000	-1.02700200
	H	1.79724400	-0.07057900	-0.85848600
	O	2.33306500	0.54010900	-0.29786000
	O	1.78398400	0.49712400	0.87878500
	C	-1.21525700	1.58378200	-0.23914100
	H	-0.25828600	1.44265200	-0.73772500
	H	-1.78080700	2.32360300	-0.80368300
	H	-1.01717200	1.99432100	0.75200000
C1B	C	-1.42951600	0.63649500	-0.76973500
	H	-0.41444600	0.75241400	-1.15136700
	H	-2.09601200	0.84355000	-1.60880800
	C	-1.65259900	-0.81335000	-0.33535600
	H	-1.51728600	-1.47322400	-1.19336700
	H	-2.68599200	-0.93015700	-0.00175100
	C	-0.72984000	-1.27697700	0.78429400
	H	-0.75689700	-0.61219300	1.65192100
	H	-1.03252500	-2.25823300	1.16831800
	C	0.70621900	-1.42263100	0.38818800
	H	1.40781200	-1.64693300	1.20973800
	O	1.11538100	-1.34762300	-0.74836800
	H	2.01188900	0.21016800	-0.81793700
	O	2.19794700	1.09268700	-0.41628300
	O	1.57127100	1.09054100	0.72147900
	C	-1.68448800	1.65426000	0.33738600
	H	-1.61430500	2.67100500	-0.04668800
	H	-2.68144600	1.52514500	0.76344300
	H	-0.95624400	1.56683200	1.14321400
C1A	C	-2.90532500	0.60333500	-0.03542000
	H	-3.49950200	0.25230500	-0.88045100
	H	-2.37861100	1.50628100	-0.34762000
	H	-3.58938200	0.87595600	0.76717100
	C	-1.91015300	-0.46098200	0.41180300
	H	-1.33896200	-0.07083100	1.25605100
	H	-2.44213100	-1.34587300	0.77323300
	C	-0.96934300	-0.86503900	-0.71894000
	H	-0.47166700	0.02432200	-1.10948700
	H	-1.56553600	-1.26270800	-1.54419100

	C	0.07678400	-1.91162900	-0.33296700
	H	0.65253800	-2.18799300	-1.21737000
	H	-0.42839500	-2.81578600	0.01354800
	C	1.04401200	-1.45540200	0.75266500
	H	0.53141600	-1.12856000	1.66095000
	H	1.69441800	-2.27755400	1.07425300
	C	1.96505500	-0.34734400	0.34717800
	H	2.57610500	0.08549200	1.15789600
	O	2.09665700	0.05758600	-0.78556000
	H	1.30254400	1.67663100	-0.80979900
	O	0.68293700	2.31818000	-0.38670600
	O	0.36427800	1.78556900	0.75475300
M1C	C	-1.75435300	0.20776600	0.38015700
	H	-1.69735200	0.07826300	1.46351600
	H	-1.84647100	1.28063900	0.20305600
	C	-0.46460100	-0.30560600	-0.25057200
	H	-0.34184000	-1.37185800	-0.05541400
	H	-0.49078400	-0.17888700	-1.33881400
	C	0.75630900	0.41106400	0.28007400
	H	0.86520800	0.30811000	1.35903300
	O	0.81598900	1.74853800	-0.02737200
	H	0.57078200	1.88103000	-0.94817900
	O	1.95399800	-0.19814100	-0.30391600
	O	2.16306400	-1.38102000	0.17524700
	C	-2.97898600	-0.51857900	-0.16301300
	H	-2.91437300	-1.58949700	0.03162900
	H	-3.89456700	-0.14834200	0.29532800
	H	-3.06522300	-0.38234600	-1.24171400
M1B	C	2.59581600	-0.43430800	-0.18256500
	H	3.33713100	-1.07549900	0.29701400
	H	2.59505500	-0.70441900	-1.24193500
	C	1.22445200	-0.74518900	0.41484800
	H	1.23828700	-0.52490200	1.48641900
	H	1.01967300	-1.81320000	0.32044800
	C	0.09353500	0.04400400	-0.23798000
	H	0.19819300	1.11174100	-0.04739500
	H	0.10529000	-0.09413800	-1.32570300
	C	-1.26230800	-0.38255200	0.27810100
	H	-1.35439900	-0.26338500	1.35699900
	O	-1.62123600	-1.66998800	-0.03931600
	H	-1.40642600	-1.84885400	-0.95988300
	O	-2.28712000	0.48414400	-0.31028500
	O	-2.22701400	1.68209000	0.17299100
	C	3.01258900	1.02469600	-0.02619700
	H	4.03213200	1.18045300	-0.37584600
	H	2.36611500	1.69244500	-0.59516100
	H	2.96740800	1.32988900	1.02067900

M1A	C	2.91698200	1.16206700	0.65472700
	H	3.48990900	0.60544000	1.39862700
	H	1.96249700	1.43290800	1.10762900
	H	3.45162800	2.08690300	0.44325100
	C	2.72504200	0.33445900	-0.61212100
	H	2.10542200	0.88825000	-1.32130200
	H	3.68944900	0.19398700	-1.10314300
	C	2.11181200	-1.04179100	-0.34891400
	H	2.81556900	-1.63725900	0.23787400
	H	1.98305200	-1.56388900	-1.30073200
	C	0.77138200	-1.01168300	0.38607100
	H	0.90932800	-0.62246600	1.39799800
	H	0.40301500	-2.03261700	0.50071100
	C	-0.28071800	-0.17059900	-0.32983500
	H	0.00343600	0.88198000	-0.34610500
	H	-0.38855200	-0.49140200	-1.37280600
	C	-1.63271600	-0.27062900	0.33955200
	H	-1.60549200	0.04161600	1.38291300
	O	-2.21346800	-1.51415600	0.28306000
	H	-2.11168000	-1.87964800	-0.60102900
	O	-2.56160100	0.64518500	-0.32868600
	O	-2.27221700	1.87962700	-0.07446900
TS2B	C	0.59329600	1.26856600	-0.25614800
	H	1.04772700	2.23994900	-0.06637800
	H	0.64891500	1.09848700	-1.33386400
	O	0.71243100	-0.97076000	0.70255900
	O	0.22723800	-1.44457400	-0.50133000
	C	-0.87108700	1.23755100	0.19759100
	H	-1.33742200	2.20848200	0.00569600
	H	-0.91832400	1.07638500	1.27715100
	C	-1.66796800	0.16427400	-0.51092400
	H	-0.79382500	-0.80988600	-0.62042800
	H	-1.84433700	0.38905400	-1.56360300
	C	-2.84927800	-0.40603400	0.22129700
	H	-3.58304400	0.37942500	0.43165600
	H	-2.53725500	-0.82599300	1.17844800
	O	2.63793400	-0.03727300	-0.20304300
	H	2.42332700	-0.41327600	-1.06320800
	C	1.44736400	0.22120300	0.45775500
	H	1.70759300	0.54893100	1.46479600
	H	-3.34813800	-1.18406100	-0.35318400
TS2A	C	1.70170000	0.07030400	0.34615300
	C	1.02482000	1.07905600	-0.57078500
	H	1.80091900	1.78035600	-0.87810200
	H	0.70468800	0.55838300	-1.47585400
	O	0.78780200	-0.89286300	0.85971900
	O	0.20029700	-1.56316400	-0.19373600
	C	-0.14220500	1.85246100	0.04696400
	H	-0.48993600	2.57029500	-0.69904300

	H	0.22021700	2.44285800	0.89147900
	C	-1.33395100	1.00567100	0.50974600
	H	-2.17974300	1.67245700	0.71905900
	H	-1.10432000	0.51240700	1.45697800
	C	-1.77859600	-0.03935700	-0.47746400
	H	-0.77656900	-0.90377300	-0.43948300
	H	-1.75808200	0.28628100	-1.51893200
	C	-2.99407900	-0.84085700	-0.09839600
	H	-3.88279400	-0.20192600	-0.08151000
	H	-3.18123400	-1.65136400	-0.80068200
	H	-2.87724300	-1.26905300	0.89755500
	O	2.77927300	-0.54955000	-0.27201900
	H	2.43738500	-1.06328900	-1.01135100
	H	2.08160700	0.54731600	1.25086300
M2B	C	0.01197900	-1.28492800	0.36319700
	H	-0.13837600	-2.11039100	-0.33481200
	H	0.49640300	-1.68996900	1.25615700
	O	1.25158200	0.67231600	0.67085300
	O	1.95501200	1.72103200	0.03482800
	C	-1.32880800	-0.64823100	0.72860300
	H	-1.16015500	0.18683600	1.41256000
	H	-1.91720500	-1.38529800	1.29315400
	C	-2.09513200	-0.17896800	-0.45928900
	H	2.80999600	1.31088900	-0.15431600
	H	-2.07296300	-0.79160700	-1.35278600
	C	-3.15580200	0.85220000	-0.31771900
	H	-2.79181200	1.71104900	0.25089800
	H	-4.02773500	0.46597100	0.22683500
	O	2.15496200	-0.91352600	-0.73353200
	H	2.47884700	-1.49668900	-0.04001000
	C	0.96871300	-0.30961600	-0.29456800
	H	0.53495700	0.17151400	-1.17209800
	H	-3.51011200	1.20637300	-1.28411600
M2A	C	1.61207700	-0.26726100	-0.28056600
	O	1.32522100	0.87298400	0.49091700
	O	1.89919500	1.99329500	-0.15473900
	H	2.84553500	1.84427100	-0.02330500
	H	1.24234800	-2.32831300	-0.02007300
	H	0.81738600	-1.34065200	1.37753200
	C	0.76766300	-1.39520600	0.28535100
	C	-0.68645700	-1.38977100	-0.18249500
	H	-1.17940900	-2.27173500	0.23273700
	H	-0.71542400	-1.50749400	-1.26887900
	C	-1.48996800	-0.15034400	0.20818500
	H	-1.07777000	0.73901400	-0.27712300
	H	-1.35382500	0.03661800	1.28507400
	C	-2.93493400	-0.27634400	-0.12101800
	H	-3.37735600	-1.26469200	-0.13568000
	C	-3.82419500	0.91398100	-0.07844400

	H	-4.80426400	0.70720200	-0.50494800
	H	-3.98355600	1.26434100	0.95001700
	H	-3.38303200	1.75333800	-0.62180500
	O	2.98974100	-0.52882800	-0.24541700
	H	3.21172900	-0.88482300	0.62069900
	H	1.37926800	-0.05701300	-1.32641300
C3A	C	2.12816300	-0.41368200	-0.19591900
	O	2.06475200	0.92593400	0.23067700
	O	2.67368800	1.73107700	-0.76010500
	H	3.60736300	1.49452800	-0.67339300
	H	1.55211300	-2.24586800	0.68095800
	H	1.43111900	-0.86103700	1.76533800
	C	1.23586900	-1.20442100	0.74441800
	C	-0.25563400	-1.11313500	0.42324200
	H	-0.79858500	-1.75117400	1.12346500
	H	-0.43388500	-1.53712900	-0.56679800
	C	-0.82691800	0.30113900	0.48535500
	H	-0.41362300	0.92156200	-0.31175000
	H	-0.53386700	0.77907300	1.42402200
	C	-2.34356100	0.34688700	0.40183700
	H	-2.79669200	-0.27886000	1.17170100
	C	-2.89766200	1.75465800	0.42241700
	H	-3.98304300	1.74611500	0.34531600
	H	-2.61570800	2.24615000	1.35220000
	H	-2.49093900	2.33236800	-0.40711300
	O	3.46059100	-0.84744200	-0.20027100
	H	3.74522600	-0.97777300	0.70977900
	H	1.79530400	-0.47265600	-1.23412900
	O	-2.76311600	-0.23094600	-0.86588800
	O	-2.97420500	-1.50662100	-0.78787300
TS3A	C	-1.58473400	0.27622300	-0.24101200
	O	-1.47954100	-0.81873500	0.67545600
	O	-1.41530900	-1.97442500	-0.02135600
	H	-0.23260900	-2.16043100	-0.02032200
	H	-1.98747200	2.23741300	0.43639200
	H	-1.02190800	1.28402300	1.55307100
	C	-1.15865800	1.53402400	0.49973900
	C	0.10676100	2.18742500	-0.06107500
	H	0.15694700	3.20448800	0.32995500
	H	0.00715100	2.28748100	-1.14591100
	C	1.44175600	1.51161000	0.26329800
	H	1.57291200	1.43470400	1.34643300
	H	2.24344100	2.15861600	-0.09710200
	C	1.68228600	0.12656900	-0.32505600

	H	1.18848800	0.00573700	-1.29262600
	C	3.15575000	-0.21612400	-0.45185300
	H	3.27385500	-1.25335200	-0.75817200
	H	3.62531900	0.42676700	-1.19537900
	H	3.65657600	-0.06942300	0.50532500
	O	-2.89198900	0.40287600	-0.68618100
	H	-3.13280800	-0.40240800	-1.15550600
	H	-0.92123500	0.02853900	-1.07384200
	O	1.07254500	-0.80645400	0.58737900
	O	0.92834100	-2.01582600	0.00263200
M3A	C	-1.80129600	0.04544100	0.53112000
	O	-2.93284800	-0.66670900	-0.08573000
	O	-3.84050700	0.15514500	-0.49906700
	H	1.73630800	-2.40426500	-0.52961300
	H	-0.59712500	-0.03636200	-1.22404500
	H	-1.74593200	1.29380100	-1.16134200
	C	-1.02219100	0.72926000	-0.57319300
	C	0.05471000	1.69102000	-0.06001600
	H	-0.41660500	2.38519800	0.64007600
	H	0.39264000	2.29880800	-0.90297700
	C	1.28375400	1.07922300	0.62043100
	H	0.99233200	0.36548600	1.39173500
	H	1.82527000	1.87756900	1.13295600
	C	2.28325000	0.42430300	-0.32437000
	H	2.55279500	1.13292300	-1.11333900
	C	3.53369000	-0.06025600	0.38654400
	H	4.20122100	-0.56082300	-0.31388900
	H	4.06494600	0.78348900	0.82471000
	H	3.27549800	-0.75075200	1.18828100
	O	-1.10960900	-0.89139100	1.24914600
	H	-0.45488600	-1.32061900	0.68233400
	H	-2.25716700	0.75585700	1.22153800
	O	1.69554100	-0.61968700	-1.10715700
	O	1.24232400	-1.63663900	-0.22213300
TS4A	C	1.94781200	-0.32697900	0.21695600
	O	0.95111100	-1.21180100	0.78226100
	O	0.18414900	-0.63247300	1.76263500
	H	-0.50040100	-2.09543200	-0.30614800
	H	1.44990900	1.38551600	1.41450400
	H	2.63102900	1.62826700	0.14656400
	C	1.66705800	1.16843800	0.36923500
	C	0.62817500	1.81483900	-0.55684700
	H	0.73473900	1.42103000	-1.56855300
	H	0.87928300	2.87319800	-0.63281400
	C	-0.83578100	1.73449100	-0.12035900
	H	-1.45657400	2.25261900	-0.85965600
	H	-0.97346500	2.26078800	0.82679500
	C	-1.37245600	0.33690200	0.06346600
	H	-0.70463700	-0.12894100	1.08781500

	C	-2.83350800	0.19919000	0.39750200
	H	-3.09536900	-0.83588500	0.59704900
	H	-3.06676200	0.80181000	1.27358200
	H	-3.43510300	0.55662000	-0.44262800
	O	2.09520600	-0.74609500	-1.09136500
	H	1.24926500	-0.62119100	-1.53967700
	H	2.88676100	-0.55861800	0.72169700
	O	-0.93302800	-0.43128100	-1.00801600
	O	-1.27324800	-1.79098300	-0.81279500
P	C	-1.86864600	-0.52036200	0.15414900
	O	-1.53334500	0.60860700	0.93788100
	O	-1.30440700	1.69381400	0.05224900
	H	-1.09911800	-1.82279300	-1.31415600
	H	-0.35358200	-0.23930600	-1.34069000
	C	-0.69726500	-1.03531100	-0.67629800
	C	0.45359700	-1.61374800	0.14827100
	H	1.12130500	-2.16425500	-0.51824500
	H	0.05624400	-2.34857700	0.85163900
	C	1.28398200	-0.59416300	0.95563100
	H	2.02857600	-1.13365200	1.54196200
	H	0.63687100	-0.03181200	1.62511900
	C	1.97480500	0.37027000	0.02623400
	H	-0.33046900	1.70071700	-0.02692200
	C	3.35028800	0.00278800	-0.45772400
	H	3.66589600	0.67040300	-1.25329400
	H	4.04640400	0.07404700	0.38036900
	H	3.36747500	-1.03364400	-0.79713400
	O	-2.98880700	-0.27051800	-0.62868400
	H	-2.82254300	0.55219200	-1.10253800
	H	-2.15587600	-1.26023300	0.90558900
	O	1.43384100	1.39060600	-0.34310600
OH	H	0.00000000	0.00000000	-0.86302900
	O	0.00000000	0.00000000	0.10787900

Table S24. Absolute energies in hartrees

Species	Methods	Total energies (a.u.)
HO_2	CCSD(T)-F12a/cc-pVTZ-F12	-150.78477083
	CCSD(T)-F12a/cc-pVDZ-F12	-150.76418048
	M06-2X /MG3S	150.900055
	M11-L/MG3S	-150.90327500
C_4H_8O	CCSD(T)-F12a/cc-pVTZ-F12	-232.17432822
	CCSD(T)-F12a/cc-pVDZ-F12	-232.14694116
	M06-2X /MG3S	232.425625
	M11-L/MG3S	-232.48220800
$C_5H_{10}O$	CCSD(T)-F12a/cc-pVTZ-F12	-271.43229796
	CCSD(T)-F12a/cc-pVDZ-F12	-271.40054289
	M06-2X /MG3S	271.73146
	M11-L/MG3S	-271.80124100
$C_6H_{12}O$	CCSD(T)-F12a/cc-pVTZ-F12	-310.69014362
	CCSD(T)-F12a/cc-pVDZ-F12	-310.65401591
	M06-2X /MG3S	-311.03714400
	M11-L/MG3S	-311.12010900
C1C	CCSD(T)-F12a/cc-pVTZ-F12	-382.97325135
	CCSD(T)-F12a/cc-pVDZ-F12	-382.92514161
	M06-2X /MG3S	-383.34276500
	M11-L/MG3S	-383.39956700
C1B	CCSD(T)-F12a/cc-pVTZ-F12	-422.23071584
	CCSD(T)-F12a/cc-pVDZ-F12	-422.17824229
	M06-2X /MG3S	-422.64868000
	M11-L/MG3S	-422.71800000
C1A	CCSD(T)-F12a/cc-pVTZ-F12	-461.48880852
	CCSD(T)-F12a/cc-pVDZ-F12	-461.43197836
	M06-2X /MG3S	-461.95510000
	M11-L/MG3S	-462.03716100
TS1C	CCSD(T)-F12a/cc-pVTZ-F12	-382.96281130
	CCSD(T)-F12a/cc-pVDZ-F12	-382.91471564
	M06-2X /MG3S	-383.33195700
	M11-L/MG3S	-383.38767500
TS1B	CCSD(T)-F12a/cc-pVTZ-F12	-422.22071804
	CCSD(T)-F12a/cc-pVDZ-F12	-422.16825712
	M06-2X /MG3S	-422.63773300

	M11-L/MG3S	-422.70667400
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	CCSD(T)-F12a/cc-pVDZ-F12	-461.42172361
	M06-2X /MG3S	-461.94344400
	M11-L/MG3S	-462.02557800
M1C	CCSD(T)-F12a/cc-pVTZ-F12	-382.98427872
	CCSD(T)-F12a/cc-pVDZ-F12	-382.93604158
	M06-2X /MG3S	-383.35517900
	M11-L/MG3S	-383.40595900
M1B	CCSD(T)-F12a/cc-pVTZ-F12	-422.24132412
	CCSD(T)-F12a/cc-pVDZ-F12	-422.18872183
	M06-2X /MG3S	-422.66031300
	M11-L/MG3S	-422.72395800
M1A	CCSD(T)-F12a/cc-pVTZ-F12	-461.49776390
	CCSD(T)-F12a/cc-pVDZ-F12	-461.44175597
	M06-2X /MG3S	-461.96602600
	M11-L/MG3S	-462.04216200
TS2B	CCSD(T)-F12a/cc-pVTZ-F12	-422.20485011
	CCSD(T)-F12a/cc-pVDZ-F12	-422.15198348
	M06-2X /MG3S	-422.62374300
	M11-L/MG3S	-422.69264900
TS2A	CCSD(T)-F12a/cc-pVTZ-F12	-461.46458422
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	M06-2X /MG3S	-461.93244200
	M11-L/MG3S	-462.01315900
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	M06-2X /MG3S	-422.64330000
	M11-L/MG3S	-422.71178800
M2A	CCSD(T)-F12a/cc-pVTZ-F12	-461.48029127
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	M06-2X /MG3S	-461.94702400
	M11-L/MG3S	-462.02884100
C3A	CCSD(T)-F12a/cc-pVDZ-F12	-611.66312653
	M06-2X /MG3S	-612.32775100
TS3A	CCSD(T)-F12a/cc-pVDZ-F12	-611.63268729
	M06-2X /MG3S	-612.29906800

M3A	CCSD(T)-F12a/cc-pVDZ-F12	-611.66202340
	M06-2X /MG3S	-612.32740400
TS4A	CCSD(T)-F12a/cc-pVDZ-F12	-611.62775038
	M06-2X /MG3S	-612.29441600
M4A	CCSD(T)-F12a/cc-pVDZ-F12	-536.04674838
	M06-2X /MG3S	-536.64187700
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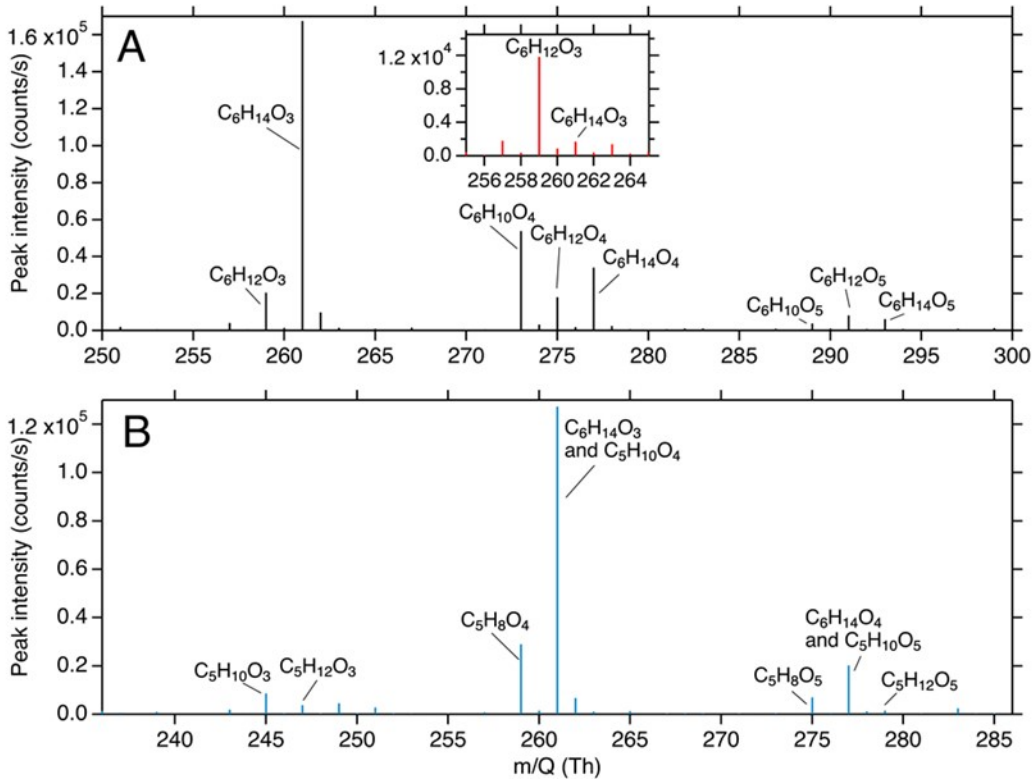

Figure S1. Example mass spectrum of gas-phase products of (A) hexanal + HO_2 and (B) pentanal + HO_2 in the presence of O_3, TME (C_6H_{12}), and methanol (see experimental conditions described in the main text). In (A), the high abundance of $C_6H_{14}O_3$ is likely from both TME and hexanal, leading to ambiguity in confirming the hexanal + HO_2 reaction. But in the insert of (A), the mass spectrum is from ozonolysis of a-pinene ($C_{10}H_{16}$) + hexanal + methanol, and it shows a $C_6H_{14}O_3$ peak, indicative of the hexanal + HO_2 chemistry. Under similar conditions but without hexanal (i.e., control conditions of a-pinene + O_3 + methanol), the $C_6H_{14}O_3$ peak was not present.

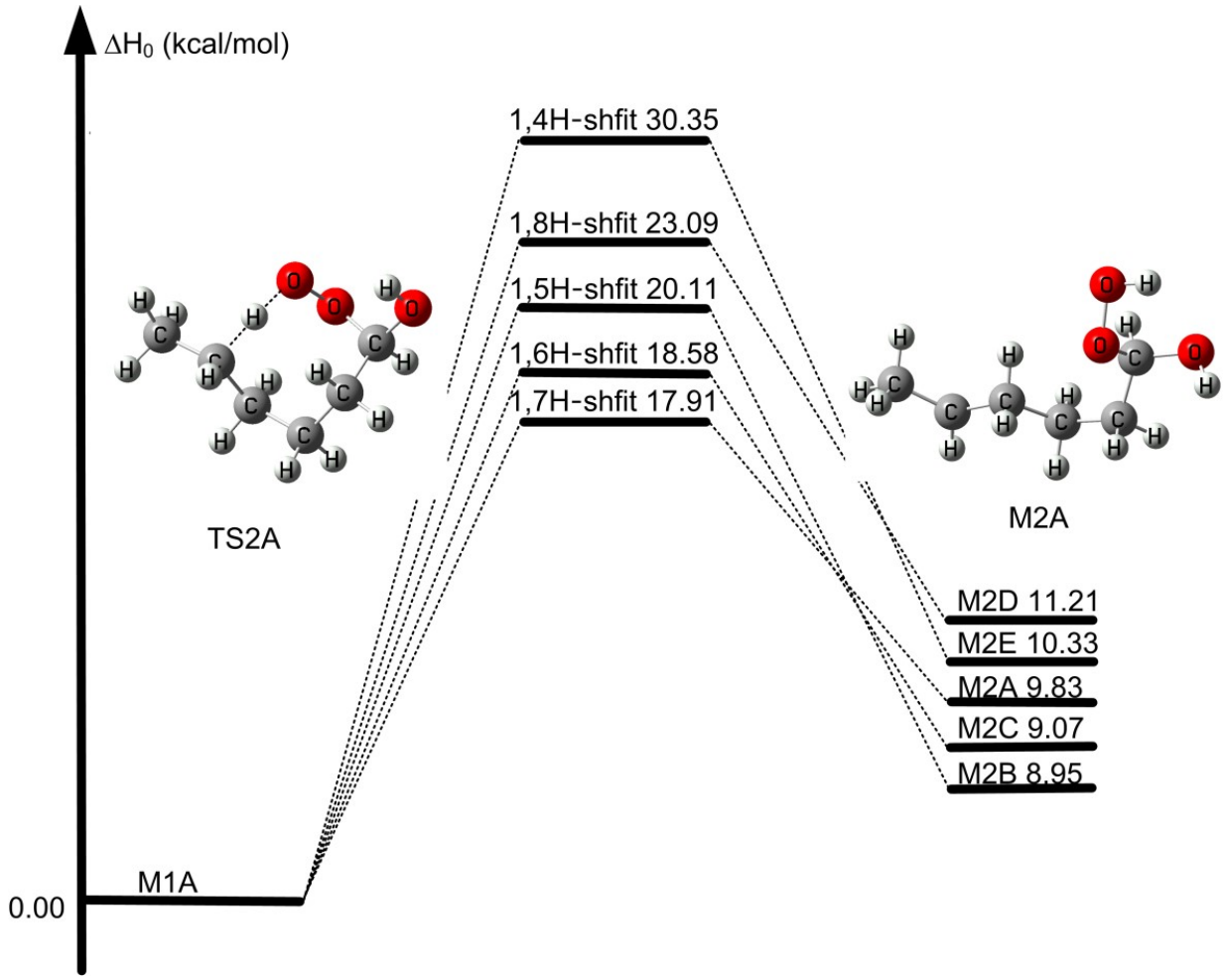

Figure S2. The relative enthalpies of all the H-shift reactions of the adduct M1A ($C_6H_{13}O_5$) at the CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S level with the standard scale factor at 0 K.

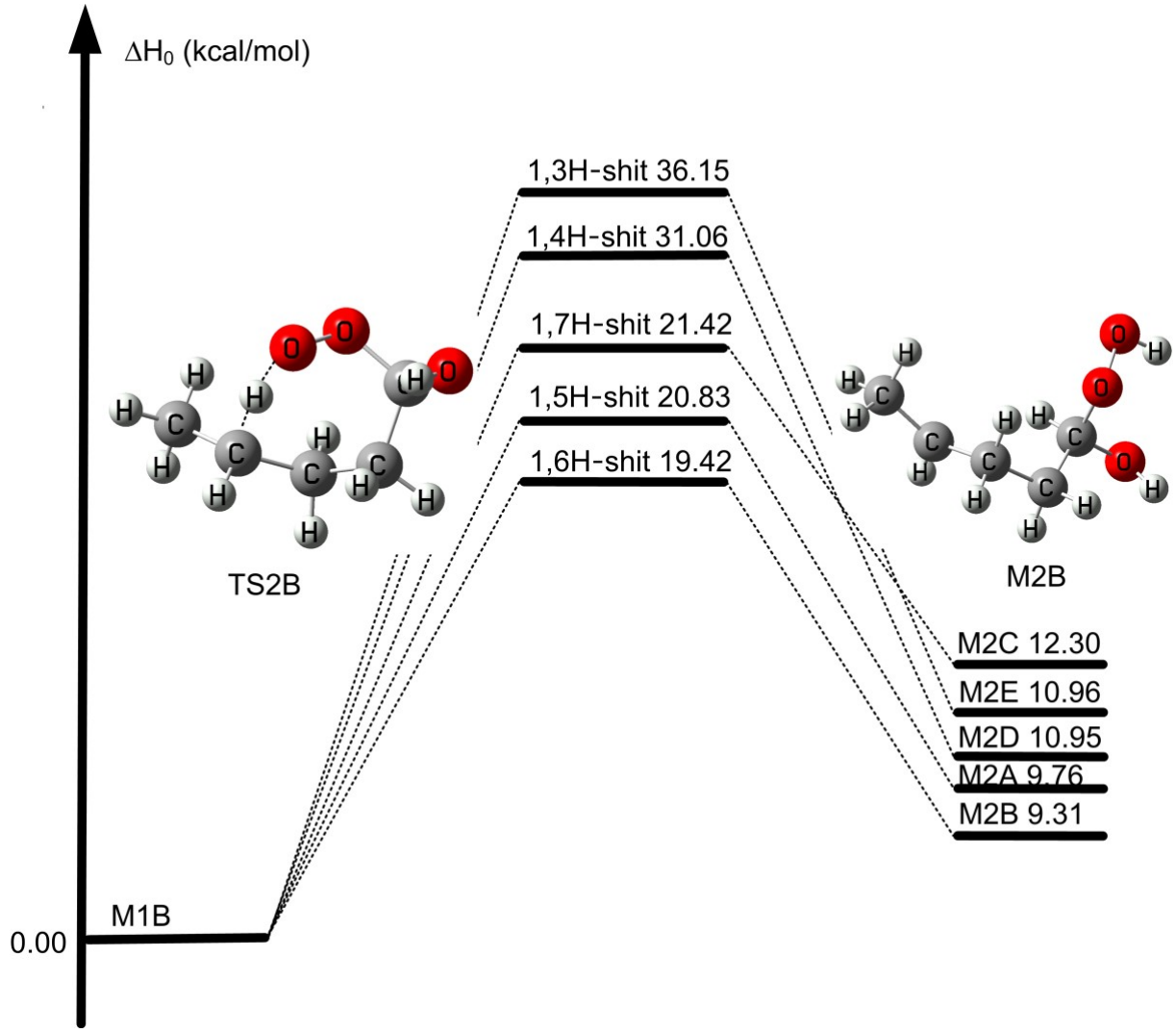

Figure S3. The relative enthalpies of all the H-shift reactions of the adduct M1B ($C_5H_{11}O_5$) at the CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S level with the standard scale factor at 0 K.

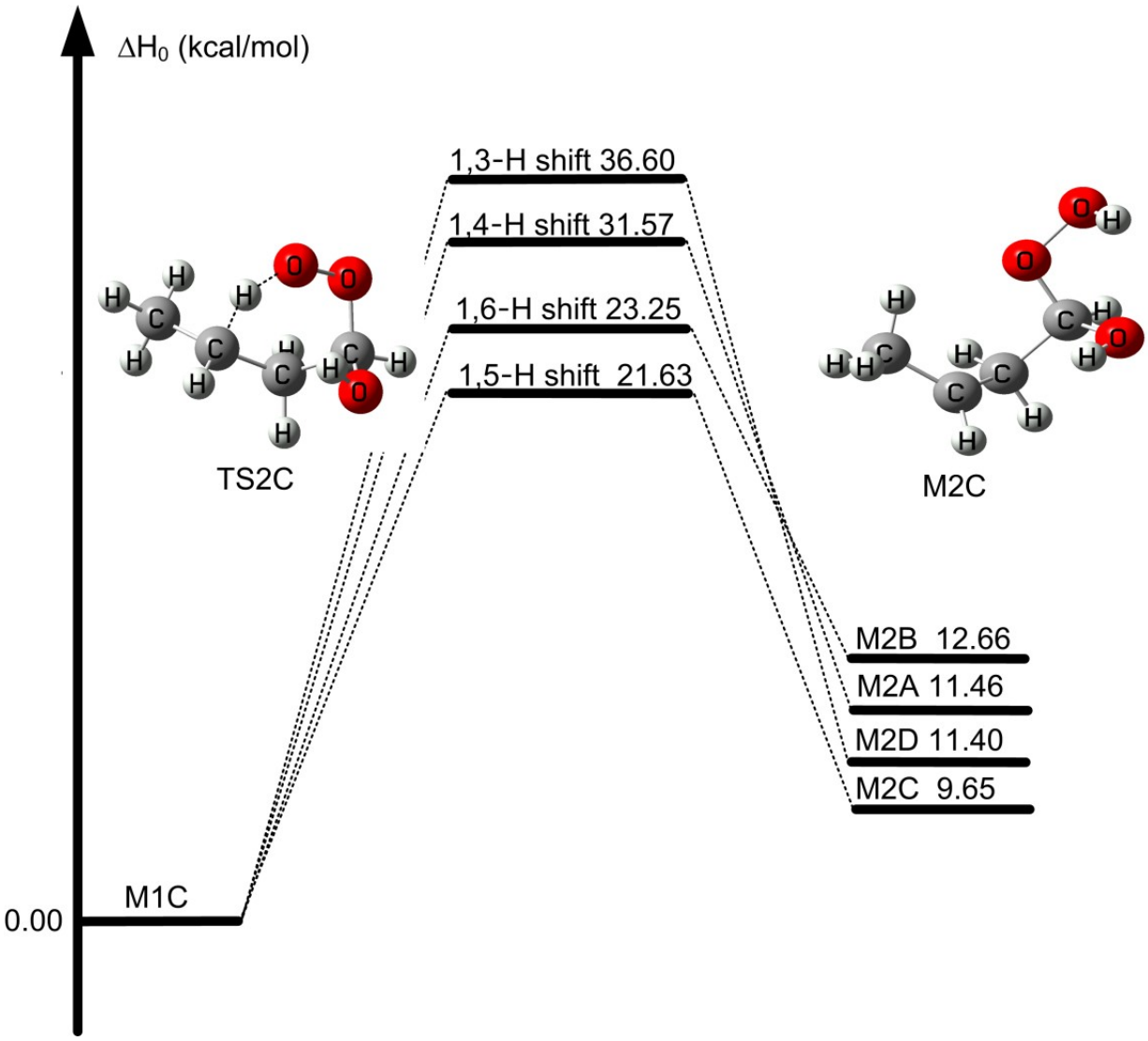

Figure S4. The relative enthalpies of all the H-shift reactions of the adduct M1C ($C_4H_9O_5$) at the CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S level with the standard scale factor at 0 K.

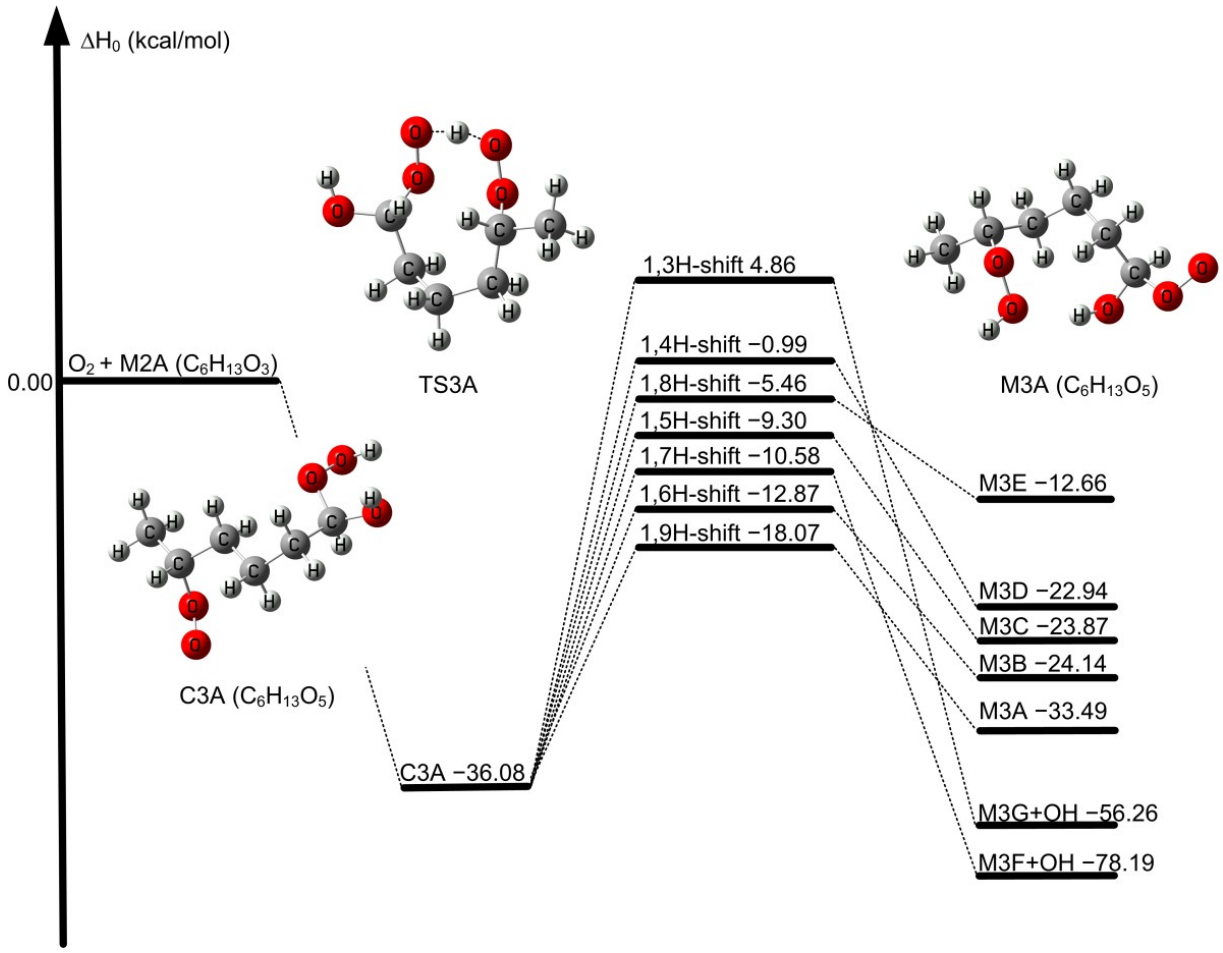

Figure S5. The relative enthalpies of all the H-shift reactions of the adduct C_3A ($C_6H_{13}O_5$) at the CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S level with the standard scale factor at 0 K.

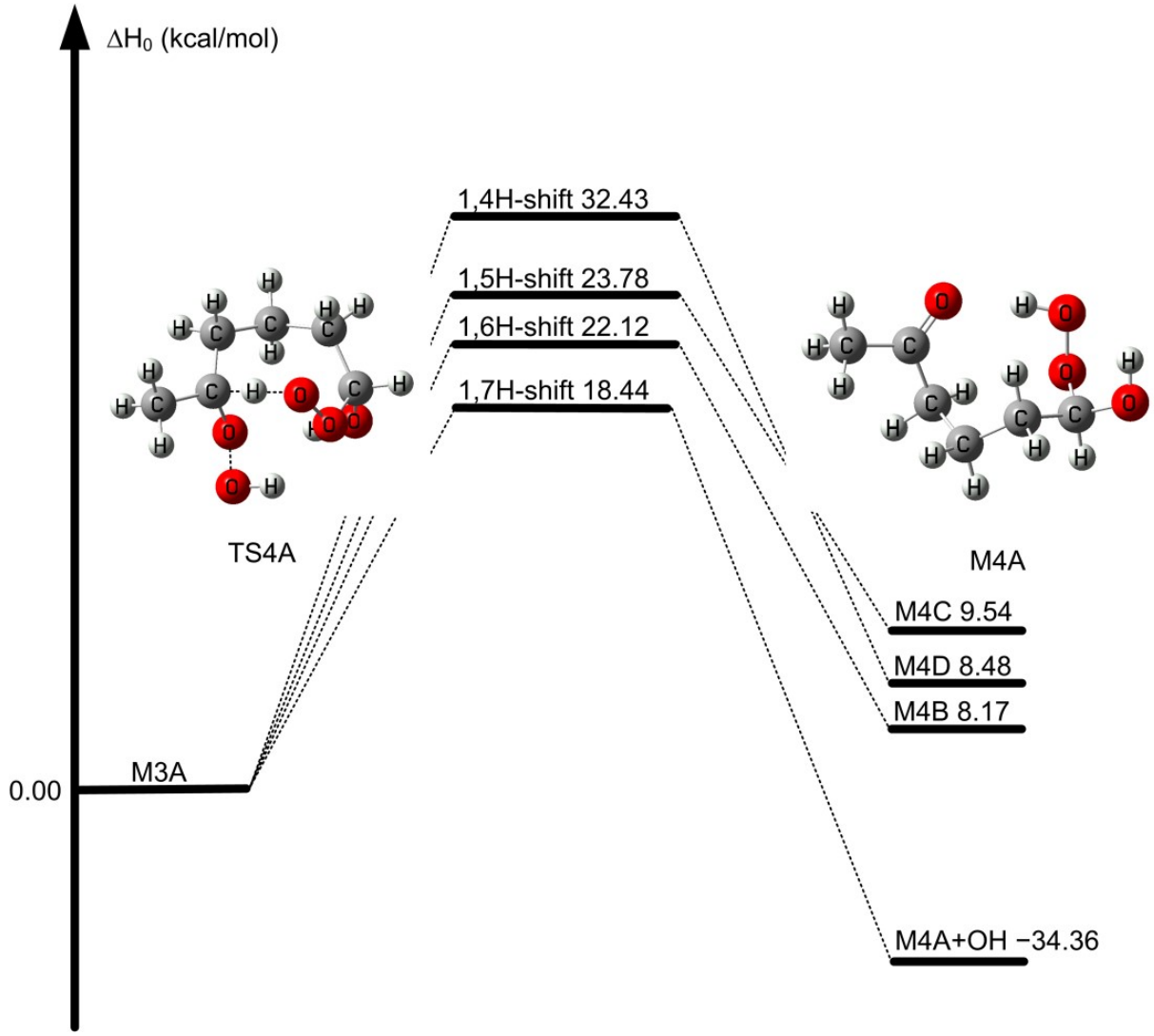

Figure S6. The relative enthalpies of all the H-shift reactions of the adduct M3A ($C_6H_{13}O_5$) at the CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S level with the standard scale factor at 0 K.

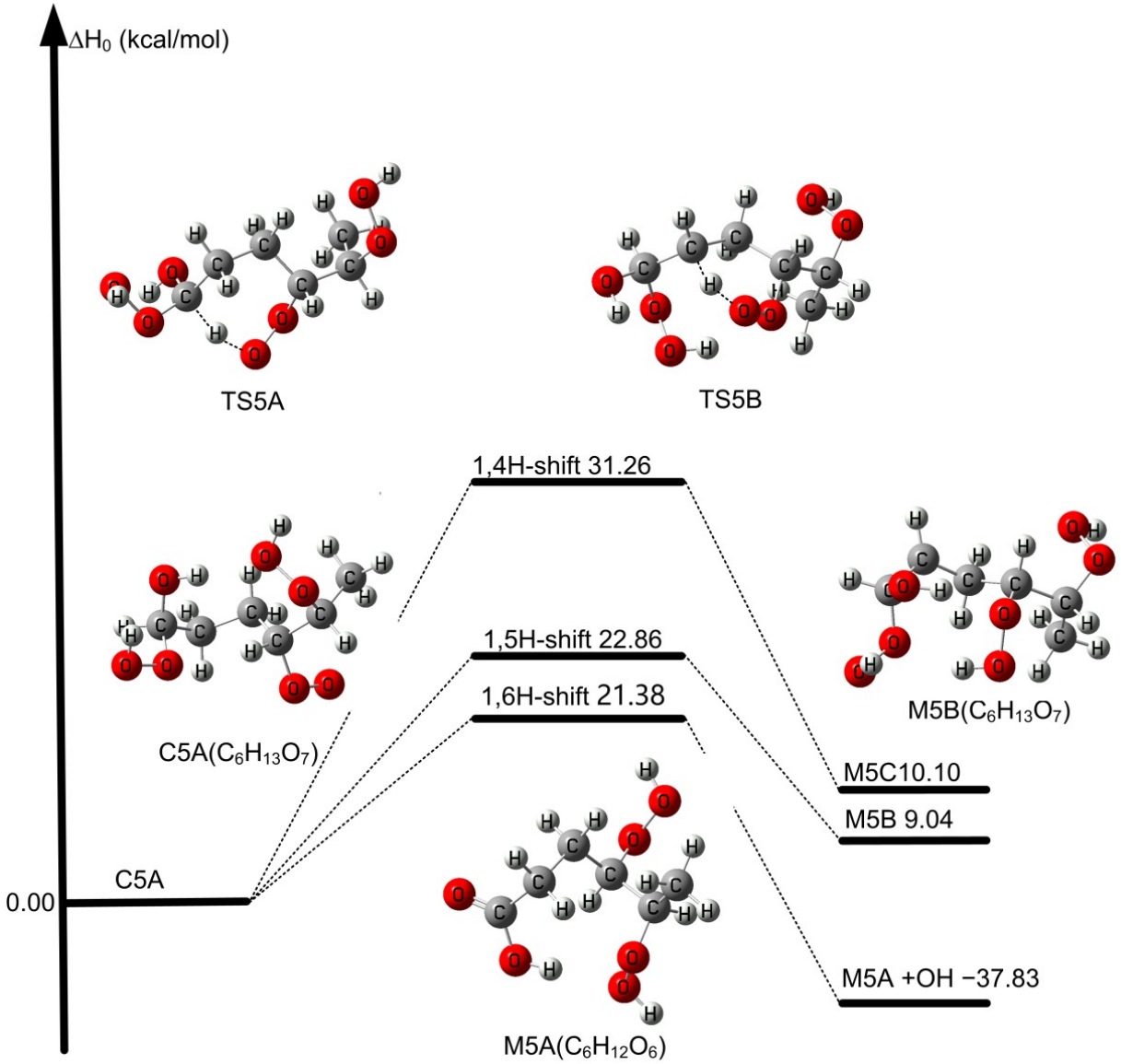

Figure S7. The relative enthalpies of all the H-shift reactions of the adduct C5A ($C_6H_{13}O_7$) at the CCSD(T)-F2a/cc-pVDZ-F12//M06-2X/MG3S level with the standard scale factor at 0 K.

Input file for MESS for the bimolecular reaction of HO_2 +$C_5H_{11}CHO$

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290. 298. 300. 310. 320. 330. 340. 350.
PressureList[bar]                     0.0316 0.1 0.178 0.316 0.562 1.    1.01325 1.78 3.16
5.62 10. 31.6 50. 100. 1000.
EnergyStepOverTemperature             .2
ExcessEnergyOverTemperature           30
ModelEnergyLimit[kcal/mol]            400
CalculationMethod                     direct
   WellCutoff                         10
   ChemicalEigenvalueMax              .2
   ChemicalEigenvalueMin              1.e-10
! Model Section
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      Exponential
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      End
   CollisionFrequency
      LennardJones
         Epsilons[1/cm]               82.       227.11
         Sigmas[angstrom]             3.74      4.45
         Masses[amu]                   28.       133.08    ! N2      HO2+C6H12O

      End
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            C                      -0.96934300     -0.86503900     -0.71894000
            H                      -0.47166700      0.02432200     -1.10948700
            H                      -1.56553600     -1.26270800     -1.54419100
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            H                       0.65253800     -2.18799300     -1.21737000
            H                      -0.42839500     -2.81578600      0.01354800
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            H                       1.69441800     -2.27755400      1.07425300
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            H                       1.30254400     1.67663100    -0.80979900
            O                       0.68293700     2.31818000    -0.38670600
            O                       0.36427800     1.78556900     0.75475300
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              SymmetryFactor                  1
            End
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           259.43 274.76 291.17 344.18 461.87 559.30 661.69 707.81 743.96
           818.87 853.72 904.03 952.97 967.62 1034.93 1060.53 1097.39
          1145.38 1148.45 1227.54 1249.67 1300.64 1303.62 1325.69
          1336.68 1382.89 1395.30 1408.17 1415.52 1430.00
         1451.29 1486.57 1492.91 1499.55 1505.95 1513.09
         1541.11 1815.62 2983.31 3041.07 3046.23 3057.16 3058.74
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          End
        End
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             C                      2.72504200     0.33445900    -0.61212100
             H                      2.10542200     0.88825000    -1.32130200
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             C                      2.11181200    -1.04179100    -0.34891400
             H                      2.81556900    -1.63725900     0.23787400
             H                      1.98305200    -1.56388900    -1.30073200
             C                      0.77138200    -1.01168300     0.38607100
             H                      0.90932800    -0.62246600     1.39799800
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             C                     -0.28071800    -0.17059900    -0.32983500
             H                      0.00343600     0.88198000    -0.34610500
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             C                     -1.63271600    -0.27062900     0.33955200
             H                     -1.60549200     0.04161600     1.38291300
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             H                     -2.11168000    -1.87964800    -0.60102900
             O                     -2.56160100     0.64518500    -0.32868600
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      965.51 993.20 1018.00 1039.99 1109.40 1122.94 1138.20 1189.36 1211.95
      1259.87 1291.00 1300.49 1311.84 1327.79 1361.16 1372.01 1381.82 1391.89
      1411.63 1419.46 1434.08 1484.04 1494.10 1499.52 1505.13 1510.76 1521.11
      3032.98 3047.53 3055.86 3061.32 3062.44 3084.24 3093.51 3100.35 3118.72
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      End
    End
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          H                  4.08179500     0.54701600    -0.24194100
          C                  2.04494000    -0.19191700    -0.44111800
          H                  1.89917500     0.25455700    -1.42780100
          H                  2.35632800    -1.22585500    -0.61322600
          C                  0.71718600    -0.18411800     0.30708000
          H                  0.39720500     0.84870300     0.46310300
          H                  0.85988900    -0.62483600     1.29950300
          C                 -0.37916000    -0.94721000    -0.42984200
          H                 -0.06869400    -1.98512200    -0.56673600
          H                 -0.51056700    -0.51820200    -1.42528800
          C                 -1.71397200    -0.91557700     0.29969400
          H                 -2.42360400    -1.63911000    -0.11653300
          H                 -1.60558400    -1.19379000     1.35349800
          C                 -2.40806200     0.41944800     0.25169400
          H                 -3.33970200     0.48971700     0.84638600
          O                 -2.02881200     1.36247300    -0.38557900
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          SymmetryFactor               1
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      1410.65 1416.35 1426.26 1452.00 1485.38 1491.78 1502.02
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            SymmetryFactor                  1
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      Core          PhaseSpaceTheory
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          H                      0.85988900     -0.62483600      1.29950300
          C                     -0.37916000     -0.94721000     -0.42984200
          H                     -0.06869400     -1.98512200     -0.56673600
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        H                    -4.99201500     0.98187600     0.41461300
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        C                    -1.86403600    -0.39822600    -0.27023100
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        H                     0.51753100    -1.02506300    -1.57476900
        C                     1.97653000    -0.91930300    -0.04279800
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        O                     2.76579300     1.42769500     0.07902000
        O                     2.38066200     0.73335300    -0.91340600
      Tunneling                         Eckart
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        WellDepth[kcal/mol]             8.64
      End
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        SymmetryFactor                  1
      End
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          753.52 794.49 836.46 904.38 929.54 962.87 1045.95 1058.45
          1067.37 1079.70 1090.84 1147.40 1189.59 1234.47 1267.84
          1295.80 1331.27 1335.79 1344.85 1384.16 1395.10 1401.59
          1414.46 1419.72 1463.97 1490.37 1495.20 1506.06 1506.81
          1516.66 1668.87 1949.52 3031.12 3035.16 3048.72 3050.61
          3058.48 3059.61 3063.49 3084.98 3089.81 3112.66 3125.65 3135.29
          ZeroEnergy[kcal/mol]              -1.67 ! B2-W1-W2
        ElectronicLevels[1/cm]              1
            0       2
    End
End
```

Input file for MESS for the bimolecular reaction of HO_2 +C_4H_9CHO

```
! Global Section
TemperatureList[K]                    190. 200. 210. 220. 230. 240. 250. 260. 270. 280.
290. 298. 300. 310. 320. 330. 340. 350.
PressureList[bar]                     0.0316 0.1 0.178 0.316 0.562 1. 1.78 3.16 5.62 10.
31.6 50. 100. 1000.
EnergyStepOverTemperature             .2
ExcessEnergyOverTemperature           30
ModelEnergyLimit[kcal/mol]            400
CalculationMethod                     direct
   WellCutoff                         10
   ChemicalEigenvalueMax              .2
   ChemicalEigenvalueMin              1.e-11
! Model Section
Model
   EnergyRelaxation
      Exponential
         Factor[1/cm]                 300
         Power                        0
         ExponentCutoff               15
      End
   CollisionFrequency
      LennardJones
         Epsilons[1/cm]               82.      222.66
         Sigmas[angstrom]             3.74     4.27
         Masses[amu]                  28.      119.07    ! N2     HO2+C5H10O

      End
!Species
   Well        W1        # C1B              CCSD(t)
      Species
         RRHO
          Geometry[angstrom]          19
            C                    -1.42951600     0.63649500    -0.76973500
            H                    -0.41444600     0.75241400    -1.15136700
            H                    -2.09601200     0.84355000    -1.60880800
            C                    -1.65259900    -0.81335000    -0.33535600
            H                    -1.51728600    -1.47322400    -1.19336700
            H                    -2.68599200    -0.93015700    -0.00175100
            C                    -0.72984000    -1.27697700     0.78429400
            H                    -0.75689700    -0.61219300     1.65192100
            H                    -1.03252500    -2.25823300     1.16831800
            C                     0.70621900    -1.42263100     0.38818800
            H                     1.40781200    -1.64693300     1.20973800
            O                     1.11538100    -1.34762300    -0.74836800
            H                     2.01188900     0.21016800    -0.81793700
            O                     2.19794700     1.09268700    -0.41628300
            O                     1.57127100     1.09054100     0.72147900
            C                    -1.68448800     1.65426000     0.33738600
```

```
        H                    -1.61430500      2.67100500     -0.04668800
        H                    -2.68144600      1.52514500      0.76344300
        H                    -0.95624400      1.56683200      1.14321400
        Core         RigidRotor
          SymmetryFactor                1
        End
        Frequencies[1/cm]                51
     58.18 73.04 92.15 107.97 150.54 189.50 228.78 250.98
     279.55 285.08 340.87 424.54 553.85 663.44 709.31 762.72
     854.20 884.08 918.88 1003.01 1018.14 1087.50 1132.36
     1151.06 1230.76 1265.70 1304.39 1320.65 1366.84
     1387.94 1401.10 1418.85 1430.61 1449.22 1487.13
     1497.23 1506.98 1516.64 1541.41 1814.76 2987.09
     3042.83 3059.17 3064.27 3073.30 3085.66 3106.07
     3114.87 3131.94 3139.96 3425.23
        ZeroEnergy[kcal/mol]                -6.67
      End
    End
Well        W2      # M1B          CCSD(t)
    Species
      RRHO
        Geometry[angstrom]          19
          C                    2.59581600     -0.43430800     -0.18256500
          H                    3.33713100     -1.07549900      0.29701400
          H                    2.59505500     -0.70441900     -1.24193500
          C                    1.22445200     -0.74518900      0.41484800
          H                    1.23828700     -0.52490200      1.48641900
          H                    1.01967300     -1.81320000      0.32044800
          C                    0.09353500      0.04400400     -0.23798000
          H                    0.19819300      1.11174100     -0.04739500
          H                    0.10529000     -0.09413800     -1.32570300
          C                   -1.26230800     -0.38255200      0.27810100
          H                   -1.35439900     -0.26338500      1.35699900
          O                   -1.62123600     -1.66998800     -0.03931600
          H                   -1.40642600     -1.84885400     -0.95988300
          O                   -2.28712000      0.48414400     -0.31028500
          O                   -2.22701400      1.68209000      0.17299100
          C                    3.01258900      1.02469600     -0.02619700
          H                    4.03213200      1.18045300     -0.37584600
          H                    2.36611500      1.69244500     -0.59516100
          H                    2.96740800      1.32988900      1.02067900
        Core         RigidRotor
          SymmetryFactor                1
        End
        Frequencies[1/cm]                51
      45.71 79.76 112.69 133.96 170.85 257.69 274.35
      313.25 348.16 434.76 499.83 506.44 570.27 751.55
     802.18 891.25 933.37 974.06 985.95 1021.24 1098.54
     1119.85 1129.15 1211.19 1216.44 1276.86 1302.82 1311.95
```

```
      1322.58 1364.73 1372.65 1382.85 1407.64 1421.71 1433.73
      1486.13 1495.60 1503.93 1509.48 1515.68 3032.14 3048.06
      3053.72 3062.46 3092.47 3095.27 3121.41 3128.98
      3132.57 3140.00 3864.95
        ZeroEnergy[kcal/mol]                -11.42
      End
    End
  Bimolecular                           R       #
    Fragment                            C5H10O
      RRHO
        Geometry[angstrom]                  16
          C                 -1.21829900    -0.06267300     0.50915800
          H                 -0.70093600    -0.97807500     0.80005300
          H                 -1.34470200     0.53381600     1.41708400
          C                 -0.34943700     0.71113300    -0.47842800
          H                 -0.85629200     1.63762600    -0.75663200
          H                 -0.23231700     0.12394200    -1.39163700
          C                  1.02829300     1.03971900     0.07688300
          H                  1.55342100     1.77490900    -0.54276800
          H                  0.96523000     1.49536600     1.07095200
          C                  1.94785300    -0.14781900     0.17960900
          H                  2.92637200     0.05180700     0.65832200
          O                  1.69163900    -1.24586700    -0.23009100
          C                 -2.58297400    -0.40589200    -0.07493200
          H                 -3.20003800    -0.94730500     0.64092800
          H                 -3.12121600     0.49745700    -0.36619900
          H                 -2.47525000    -1.02941000    -0.96311400
        Core                            RigidRotor
          SymmetryFactor                1
        End
      Frequencies[1/cm]                 42
        81.40 116.18 156.07 245.08 261.46 278.42 415.34
        666.43 706.73 758.01 859.00 895.50 909.32 1003.29
        1039.18 1077.63 1144.67 1154.71 1243.94 1274.38
       1331.28 1334.95 1385.09 1404.84 1415.48 1426.67
      1452.11 1486.57 1498.55 1506.21 1512.59 1861.67
      2940.00 3040.09 3048.17 3058.45 3061.00 3071.87
      3092.92 3109.08 3128.71 3135.95
        ZeroEnergy[kcal/mol]            0
        ElectronicLevels[1/cm]          1
          0         2
      End
    Fragment                            HO2
      RRHO
        Geometry[angstrom]                  3
        H                 -0.87923900    -0.86675500     0.00000000
        O                  0.05495200    -0.59862600     0.00000000
        O                  0.05495200     0.70697000     0.00000000
        Core                            RigidRotor
```

```
        SymmetryFactor                1
      End
    Frequencies[1/cm]                 3
      1264.87 1469.59 3703.12
      ZeroEnergy[kcal/mol]            0
      ElectronicLevels[1/cm]          1
        0          2
    End
  GroundEnergy[kcal/mol]              0
End
!Barriers
  Barrier B1   R   W1                 # C1B
    RRHO
      Stoichiometry   C5H11O3
      Core          PhaseSpaceTheory
        FragmentGeometry[angstrom]          16
          C                      -1.21829900     -0.06267300      0.50915800
          H                      -0.70093600     -0.97807500      0.80005300
          H                      -1.34470200      0.53381600      1.41708400
          C                      -0.34943700      0.71113300     -0.47842800
          H                      -0.85629200      1.63762600     -0.75663200
          H                      -0.23231700      0.12394200     -1.39163700
          C                       1.02829300      1.03971900      0.07688300
          H                       1.55342100      1.77490900     -0.54276800
          H                       0.96523000      1.49536600      1.07095200
          C                       1.94785300     -0.14781900      0.17960900
          H                       2.92637200      0.05180700      0.65832200
          O                       1.69163900     -1.24586700     -0.23009100
          C                      -2.58297400     -0.40589200     -0.07493200
          H                      -3.20003800     -0.94730500      0.64092800
          H                      -3.12121600      0.49745700     -0.36619900
          H                      -2.47525000     -1.02941000     -0.96311400
        FragmentGeometry[angstrom]          3
          H                      -0.87923900     -0.86675500      0.00000000
          O                       0.05495200     -0.59862600      0.00000000
          O                       0.05495200      0.70697000      0.00000000
        SymmetryFactor                      1
        PotentialPrefactor[au]             20.
        PotentialPowerExponent              6.
      End
      Frequencies[1/cm]                    45
       81.40 116.18 156.07 245.08 261.46 278.42 415.34
        666.43 706.73 758.01 859.00 895.50 909.32 1003.29
        1039.18 1077.63 1144.67 1154.71 1243.94 1274.38
       1331.28 1334.95 1385.09 1404.84 1415.48 1426.67
      1452.11 1486.57 1498.55 1506.21 1512.59 1861.67
      2940.00 3040.09 3048.17 3058.45 3061.00 3071.87
      3092.92 3109.08 3128.71 3135.95
       1264.87 1469.59 3703.12
```

```
        ZeroEnergy[kcal/mol]              -6.67
        ElectronicLevels[1/cm]              1
          0          2
      End
Barrier   B2    W1 W2              # TS1B
      RRHO
        Geometry[angstrom]                19
          C                       -2.42565100    -0.26246600    -0.32608100
          H                       -2.46248100    -0.18647700    -1.41588900
          H                       -2.75651400    -1.27415100    -0.07674300
          C                       -0.98842100    -0.07413500     0.14584100
          H                       -0.94125900    -0.15406300     1.23319300
          H                       -0.65156800     0.93521100    -0.10615300
          C                       -0.03837900    -1.08994800    -0.47160100
          H                       -0.34943900    -2.10773000    -0.20911400
          H                       -0.05090200    -1.03742000    -1.56279100
          C                        1.38182500    -0.95460000    -0.00482300
          H                        2.11830800    -1.56492700    -0.54080200
          O                        1.65789400    -0.57071300     1.16887100
          H                        2.08978300     0.58310900     0.90825200
          O                        2.27783800     1.35581400     0.06745700
          O                        1.87938900     0.65181000    -0.91281700
          C                       -3.37484400     0.75621300     0.29298600
          H                       -4.39823100     0.61054200    -0.05013900
          H                       -3.37064000     0.67795700     1.38079100
          H                       -3.07521000     1.77227200     0.03337400
        Tunneling                         Eckart
          ImaginaryFrequency[1/cm]          698.22
          WellDepth[kcal/mol]               4.99
          WellDepth[kcal/mol]               9.74
        End
        Core                              RigidRotor
          SymmetryFactor                  1
        End
        Frequencies[1/cm]                 50
       63.84 67.95 103.20 145.01 171.72 243.68 274.39 311.53
      402.58 568.60 652.26 718.32 734.05 781.74 795.55
      901.77 925.54 940.04 1050.61 1057.07 1066.17 1089.55
      1144.70 1188.62 1245.66 1286.69 1316.69 1333.94
      1375.40 1385.61 1395.62 1414.96 1419.33 1464.29
     1493.92 1502.58 1505.83 1516.33 1667.84
     1949.48 3035.62 3045.09 3049.97 3059.92
     3062.36 3075.33 3088.35 3111.15 3128.68 3136.78
        ZeroEnergy[kcal/mol]              -1.68 ! B2-W1-W2
        ElectronicLevels[1/cm]            1
          0       2
      End
End
```

Input file for MESS for the bimolecular reaction of HO_2 +C_3H_7CHO

```
! Global Section
TemperatureList[K]                    190. 200. 210. 220. 230. 240. 250. 260. 270. 280.
290. 298. 300. 310. 320. 330. 340. 350.
PressureList[bar]                     0.0316 0.1 0.178 0.316 0.562 1. 1.78 3.16 5.62 10.
31.6 50. 100. 1000.
EnergyStepOverTemperature             .2
ExcessEnergyOverTemperature           30
ModelEnergyLimit[kcal/mol]            400
CalculationMethod                     direct
   WellCutoff                         10
   ChemicalEigenvalueMax              .2
   ChemicalEigenvalueMin              1.e-11
! Model Section
Model
   EnergyRelaxation
      Exponential
         Factor[1/cm]                 300
         Power                        0
         ExponentCutoff               15
      End
   CollisionFrequency
      LennardJones
         Epsilons[1/cm]               82.      206.93
         Sigmas[angstrom]             3.74     4.28
         Masses[amu]                  28.      105.06   ! N2     HO2+C4H8O

      End
!Species
   Well       W1       # C1C              CCSD(t)
      Species
         RRHO
          Geometry[angstrom]          16
            C                    -1.98464200     0.27028700    -0.14054800
            H                    -2.14086800    -0.14288900    -1.13790100
            H                    -2.97120500     0.45273900     0.28671800
            C                    -1.26986600    -0.76420900     0.71741100
            H                    -0.99007200    -0.35701600     1.69433300
            H                    -1.91065900    -1.62697700     0.93319600
            C                    -0.02160400    -1.32327800     0.10913600
            H                     0.56838400    -1.99168800     0.75900800
            O                     0.33940800    -1.11519000    -1.02700200
            H                     1.79724400    -0.07057900    -0.85848600
            O                     2.33306500     0.54010900    -0.29786000
            O                     1.78398400     0.49712400     0.87878500
            C                    -1.21525700     1.58378200    -0.23914100
            H                    -0.25828600     1.44265200    -0.73772500
            H                    -1.78080700     2.32360300    -0.80368300
            H                    -1.01717200     1.99432100     0.75200000
```

```
        Core        RigidRotor
          SymmetryFactor                1
        End
        Frequencies[1/cm]               42
    49.40 86.31 93.40 124.74 188.33 219.42 257.57 275.16
      292.20 372.86 556.43 662.35 713.53 798.23 862.95 954.40
      977.16 1064.55 1125.00 1154.30 1257.15 1299.30 1303.85
      1374.61 1396.64 1417.98 1429.17 1447.91 1490.58 1501.77
      1512.60 1541.71 1815.84 2987.92 3041.02 3068.58 3071.11
      3080.31 3111.91 3136.48 3157.43 3428.42
        ZeroEnergy[kcal/mol]            -7.13
      End
    End
Well        W2      # M1C           CCSD(t)
    Species
      RRHO
        Geometry[angstrom]          16
          C                 -1.75435300     0.20776600     0.38015700
          H                 -1.69735200     0.07826300     1.46351600
          H                 -1.84647100     1.28063900     0.20305600
          C                 -0.46460100    -0.30560600    -0.25057200
          H                 -0.34184000    -1.37185800    -0.05541400
          H                 -0.49078400    -0.17888700    -1.33881400
          C                  0.75630900     0.41106400     0.28007400
          H                  0.86520800     0.30811000     1.35903300
          O                  0.81598900     1.74853800    -0.02737200
          H                  0.57078200     1.88103000    -0.94817900
          O                  1.95399800    -0.19814100    -0.30391600
          O                  2.16306400    -1.38102000     0.17524700
          C                 -2.97898600    -0.51857900    -0.16301300
          H                 -2.91437300    -1.58949700     0.03162900
          H                 -3.89456700    -0.14834200     0.29532800
          H                 -3.06522300    -0.38234600    -1.24171400
        Core        RigidRotor
          SymmetryFactor                1
        End
        Frequencies[1/cm]               42
      79.75 101.40 116.84 179.65 251.87 284.76 351.58
      357.23 496.57 505.55 570.92 752.54 874.99 918.64
      963.67 996.15 1072.50 1116.55 1128.36 1211.87 1243.02
      1293.40 1312.27 1321.58 1361.77 1371.87 1406.24 1419.79
      1434.37 1488.93 1500.18 1507.39 1516.24 3037.72 3059.94
      3064.51 3092.51 3113.88 3127.31 3132.13 3141.57 3865.59
        ZeroEnergy[kcal/mol]           -12.05
      End
    End
  Bimolecular                       R    #
    Fragment                        C4H8O
      RRHO
```

```
      Geometry[angstrom]                 13
        C                  -1.01135400      0.40855500     -0.52911500
        H                  -1.73263600      1.19241500     -0.76296000
        H                  -0.69610300     -0.03078000     -1.47622100
        C                   0.19963900      1.03687500      0.14582500
        H                   0.54240500      1.93256700     -0.38394700
        H                  -0.03479900      1.37509600      1.16093200
        C                   1.39461800      0.12580300      0.23543700
        H                   2.25630000      0.52971600      0.80192500
        O                   1.46293000     -0.95991900     -0.27029800
        C                  -1.67006400     -0.65936300      0.33839400
        H                  -2.53510700     -1.09215500     -0.16190300
        H                  -0.97058000     -1.46464000      0.55707800
        H                  -2.00994900     -0.23408300      1.28423400
      Core          RigidRotor
        SymmetryFactor              1
      End
      Frequencies[1/cm]                33
      119.01 167.44 205.62 289.00 368.10 661.64
      708.85 797.47 859.93 950.67 971.49 1062.02
      1126.14 1154.07 1255.11 1298.82 1371.42 1390.14
      1415.11 1426.12 1451.74 1490.63 1505.21 1515.37
      1862.03 2939.23 3039.34 3062.94 3066.37 3078.37
      3110.86 3133.12 3149.35
      ZeroEnergy[kcal/mol]          0
      ElectronicLevels[1/cm]        1
        0          2
    End
  Fragment                          HO2
    RRHO
      Geometry[angstrom]                3
      H                 -0.87923900     -0.86675500      0.00000000
      O                  0.05495200     -0.59862600      0.00000000
      O                  0.05495200      0.70697000      0.00000000
      Core       RigidRotor
        SymmetryFactor              1
      End
    Frequencies[1/cm]                 3
      1264.87 1469.59 3703.12
      ZeroEnergy[kcal/mol]          0
      ElectronicLevels[1/cm]        1
        0          2
    End
  GroundEnergy[kcal/mol]            0
End
!Barriers
  Barrier B1    R    W1               # C1C
    RRHO
      Stoichiometry    C4H9O3
```

```
      Core        PhaseSpaceTheory
        FragmentGeometry[angstrom]        13
          C                -1.01135400     0.40855500    -0.52911500
          H                -1.73263600     1.19241500    -0.76296000
          H                -0.69610300    -0.03078000    -1.47622100
          C                 0.19963900     1.03687500     0.14582500
          H                 0.54240500     1.93256700    -0.38394700
          H                -0.03479900     1.37509600     1.16093200
          C                 1.39461800     0.12580300     0.23543700
          H                 2.25630000     0.52971600     0.80192500
          O                 1.46293000    -0.95991900    -0.27029800
          C                -1.67006400    -0.65936300     0.33839400
          H                -2.53510700    -1.09215500    -0.16190300
          H                -0.97058000    -1.46464000     0.55707800
          H                -2.00994900    -0.23408300     1.28423400
        FragmentGeometry[angstrom]        3
          H                -0.87923900    -0.86675500     0.00000000
          O                 0.05495200    -0.59862600     0.00000000
          O                 0.05495200     0.70697000     0.00000000
        SymmetryFactor                    1
        PotentialPrefactor[au]           20.
        PotentialPowerExponent            6.
      End
      Frequencies[1/cm]                  36
        119.01 167.44 205.62 289.00 368.10 661.64
       708.85 797.47 859.93 950.67 971.49 1062.02
       1126.14 1154.07 1255.11 1298.82 1371.42 1390.14
       1415.11 1426.12 1451.74 1490.63 1505.21 1515.37
      1862.03 2939.23 3039.34 3062.94 3066.37 3078.37
      3110.86 3133.12 3149.35 1264.87 1469.59 3703.12
      ZeroEnergy[kcal/mol]              -7.13
      ElectronicLevels[1/cm]             1
        0          2
    End
Barrier   B2    W1    W2          # TS1C
    RRHO
      Geometry[angstrom]               16
        C               -1.41617400    -0.23489900    -0.41734100
        H               -1.30440600     0.22988700    -1.39671600
        H               -0.88899100    -1.19013600    -0.46359500
        C               -0.75216300     0.64960300     0.62875000
        H               -1.25248300     1.62399700     0.67268600
        H               -0.83607900     0.21708600     1.62860700
        C                0.69536100     0.93478400     0.35247600
        H                1.24274100     1.43836600     1.15805800
        O                1.13422700     1.03795800    -0.82987000
        H                1.78251400    -0.03934300    -0.90003600
        O                2.06684300    -1.01104200    -0.33942700
        O                1.45342100    -0.77435900     0.74822300
```

```
          C                    -2.88932900     -0.46914200     -0.10649700
          H                    -3.35569500     -1.10301300     -0.85898200
          H                    -3.01342100     -0.95365200      0.86279000
          H                    -3.43626900      0.47427200     -0.07854600
        Tunneling                          Eckart
          ImaginaryFrequency[1/cm]          699.59
          WellDepth[kcal/mol]               5.44
          WellDepth[kcal/mol]               10.36
        End
        Core   RigidRotor
           SymmetryFactor                 1
        End
        Frequencies[1/cm]                 41
       73.92 85.26 134.58 221.38 247.50 280.21 347.35 571.65
       655.48 719.85 741.62 790.54 852.66 878.83 982.32 1040.00
       1065.76 1069.77 1141.45 1188.11 1262.99
       1317.16 1333.27 1384.12 1395.69 1411.53
       1418.94 1464.35 1499.38 1506.88 1514.37
       1667.75 1950.06 3035.43 3050.19 3059.98 3072.75
       3087.73 3110.90 3132.24 3139.77
        ZeroEnergy[kcal/mol]              -1.69 ! B2-W1-W2
       ElectronicLevels[1/cm]             1
         0    2
    End
End
```

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