Electronic Supplementary Material for "Competition between H_2O and $(H_2O)_2$ reactions with CH_2OO/CH_3CHOO"

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This supplementary material includes the following:

Details concerning the estimate of the water concentration error and experimental conditions for the high temperature experiments. Details of the quantum chemistry energetics, geometries obtained by QCISD(T) method, values of the rate coefficients. Discussion on the hindered rotor approximation, and discussion on effective rates as well as discussion on the water dimer equilibrium constants.

Supporting material for Experiments

1. Water concentration measurements and error estimation

The relative humidity inside the photolysis cell was calibrated at different temperatures and H_2O concentrations, using the same Rotronic sensor described in the main text against a second Rotronic sensor located upstream of the photolysis cell before the CH_2I_2 vapor was added into the gas mixture. The water concentration, $[H_2O]$, in the photolysis cell was derived by the formula below:

$$[\mathrm{H_2O}] = RH[\mathrm{H_2O}]_{\mathrm{sat}} \frac{P}{P_{\mathrm{up}}} \frac{T_{\mathrm{up}}}{T}$$

where *RH* is the relative humidity measured with the upstream Rotronic sensor, $[H_2O]_{sat}$ is the water concentration of the saturation pressure, P_{up} is the pressure at the upstream sensor, *P* and *T* are the pressure and temperature in the reactor.

The accuracy range of the relative humidity sensor (Rotronic, HC2-S; 0.1-0.2 K temperature accuracy; 0.8% relative humidity accuracy at 298 K, 1.8% above 333 K) leads to one source of uncertainty ($\varepsilon_{\mathrm{Rotronic}}$). The uncertainties in the temperature measurements *T* and T_{up} were about 0.3-0.6 K, which would cause an error (ε_T) of ~4%, estimated from the temperature dependence of the water vapor pressure (~7% per Kelvin).

The relative humidity in the photolysis cell differed by 2% or less from the value predicted by the upstream measurements; this uncertainty ($\varepsilon_{\mathrm{mix}}$) was possibly due to the incomplete gas mixing, temperature fluctuations and water adsorption/desorption from the tube walls, etc.

The main uncertainty in $[H_2O]$ (ε_{H_2O}) can be estimated with the following equation.[1,2]

$$\varepsilon_{\mathrm{H_2O}} = \sqrt{(\varepsilon_{\mathrm{mix}}\,[\mathrm{H_2O}])^2 + (\varepsilon_{\mathrm{Rotronic}}\,[\mathrm{H_2O}]_{\mathrm{sat}})^2 + (\varepsilon_{\mathrm{T}}\,[\mathrm{H_2O}])^2}\,.$$

Examples of the estimated error bars in $[H_2O]$ can be found in Figures 2 and 3 in the main text.

2. Experimental dimer rate constants

Figure S1 shows the Arrhenius plot of the bimolecular rate coefficient for $CH_2OO+(H_2O)_2$, k_{dimer}, collected from our previous study[1,2] and the present study. The experimental conditions for the present study are summarized in Table S1. The reaction rate coefficients with water dimer at higher temperatures (> 330 K) show consistency with data measured at lower temperatures (< 330 K).[2] At lower temperatures, the water monomer reaction is insignificant in comparison with the fast water dimer reaction. Within the small temperature range of 349 to 358 K, we did not observe any temperature dependence for the monomer reaction rate. Thus we report a bimolecular rate coefficient of CH_2OO+H_2O reaction as (7.3±0.8) $\times 10^{-16}$ cm^3s^{-1} for T = 349 to 358 K.

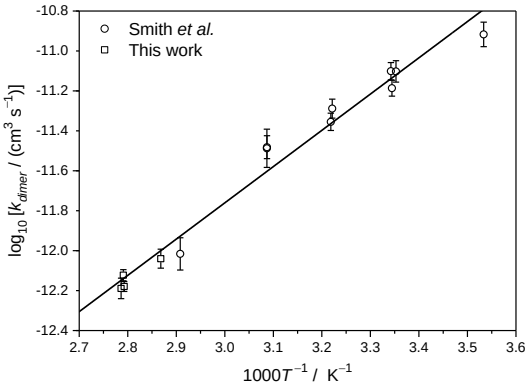


Fig. S1 The Arrhenius plot of k_{dimer}. The solid line is a linear fit to all data points. The slope gives an activation energy of -8.3 kcal mol^{-1}.

Table S1 Summary of the experiments for the temperature dependence of the CH_2OO reaction with water vapor.

Expt. #	# of multipass	Laser fluence /mJ cm^{-2}	$[CH_2I_2]$ /10^{14} cm^{-3}	P_{CH2I2} (298 K) / 10^{-3} Torr	$[CH_2OO]_0$ /10^{12} cm^{-3}	P_{O2} /Torr	P_{Total} /Torr	T_{up}§ / K	T_{cell} / K	k_0 / s^{-1}	k_{mono} / 10^{-16} cm^3s^{-1}	k_{dimer} / 10^{-12} cm^3s^{-1}

1	8	5.1	1.78	5.49	0.83	9.1	300.3	~ 315	348.7	213	7.5±0.8	0.91±0.10
2a	8	4.7	1.93	5.97	1.22	9.5	301.0	~ 315	358.9	265	7.5±0.5	0.65±0.077
2b	8	5.9	3.76	11.61	2.10	9.1	300.3	~ 315	358.3	449	6.2±0.3	0.75±0.048
2c*	8	5.0	2.98	9.21	2.14	10.6	300.4	~ 315	358.1	451	7.8±0.3	0.66±0.038
3	6	7.9	1.87	5.77	0.75	13.7	606.1	~315	343.9	361	3.9±0.9	0.96±0.17

§ T_{up} refers to the temperature of the heated water surface upstream of the reactor, which determines the H_2O saturation vapor pressure and therefore the range of H_2O concentrations possible in the reactor.

* To test the effect of OH radical in the experiment, 7.4 Torr of propane was added as OH scavenger.

Supporting material for Theoretical Simulations

1. Quantum chemistry energetics

Here we present a summary of the quantum chemistry results performed at the B3LYP/6-311+G(2d,2p) geometry. The zero point corrected energies of the 6 reaction path considered in the present study are given in Table S2.

Table S2 Zero-point corrected energies, in kcal mol^{-1}, for the three systems: CH_2OO, *anti*- and *syn*-CH_3CHOO, with three different quantum chemistry approaches. Zero-point correction was calculated with B3lYP/6-311+(2d,2p), and the zero of energy is the reactants, $CI+H_2O$ or $CI+(H_2O)_2$. All the calculation are at the geometries optimized by B3LYP/6311+G(2d,2p).

	B3LYP/6-311+G(2d,2p)			QCISD(T)/AVTZ			QCISD(T)/CBS		
Structure	vdw	ts	prd	vdw	ts	prd	vdw	ts	prd
				CH_2OO					
2a	-10.63	-7.96	-41.15	-11.56	-8.04	-45.29	-10.83	-6.61	-44.73
2b	-10.72	-7.82	-41.48	-11.76	-8.01	-46.07	-11.04	-6.52	-45.55
2c	-10.13	-6.56	-40.73	-11.25	-6.86	-45.38	-10.56	-5.35	-44.87
2d	-10.46	-7.71	-40.71	-11.46	-7.84	-44.87	-10.74	-6.40	-44.28
1a	-6.12	3.28	-38.38	-6.79	2.67	-41.58	-6.52	3.69	-41.30
1b	-6.13	2.37	-38.55	-6.80	1.83	-41.73	-6.53	2.82	-41.42
				anti-CH_3CHOO					
2a	-12.38	-6.91	-36.93	-14.46	-9.21	-43.81	-13.72	-7.47	-43.08
2b	-12.71	-7.20	-37.54	-14.83	-9.52	-44.93	-14.08	-7.74	-44.19

2c	-12.38	-5.93	-36.87	-14.46	-8.33	-44.30	-13.72	-6.53	-43.57
2d	-12.71	-6.62	-36.43	-14.83	-8.97	-43.34	-14.08	-7.22	-42.57
1a	-7.13	1.90	-34.49	-8.40	-0.26	-40.39	-8.03	0.96	-39.95
1b	-7.13	1.25	-34.39	-8.40	-0.85	-40.35	-8.03	0.34	-39.88
				syn-CH_3CHOO					
2a	-10.50	-2.99	-32.99	-12.56	-5.07	-39.22	-11.84	-3.18	-38.44
2b	-10.76	-2.95	-33.54	-12.93	-5.04	-40.14	-12.19	-3.15	-39.40
2c	-10.50	-1.30	-32.76	-12.56	-3.48	-39.42	-11.84	-1.60	-38.69
2d	-10.76	-3.23	-32.52	-12.93	-5.43	-38.78	-12.19	-3.50	-37.97
1a	-6.26	9.13	-30.19	-7.36	7.08	-35.37	-6.91	8.35	-34.89
1b	-6.26	7.56	-30.65	-7.35	5.68	-35.76	-6.91	6.96	-35.24

In Table S3, we present the results for the CH_2OO+H_2O 1b reaction channel, where we are listing the energies with respect to the van der Waals (VDW) minima. The multireference configuration interaction with perturbative quadruples correction (MRCI+Q)[3,4] as well as the multireference second order perturbation (CASPT2)[5] give barrier energies (energy differences between the VDW minima and transition state (TS) geometry) that are within 0.3 kcal mol^{-1} of the QCISD(T) results. Considering that the reaction affects 5 bonds: C1O2, O2O3,O6H7, C1O6, and O3H7; we utilized the 10 orbital 10 electron active space for the multireference calculations. The atom labels are given in section 7. The MRCI+Q correction using Davidson's scheme overestimates the barrier energies by 1 kcal mol^{-1}.

Table S3 Zero-point corrected energies, in kcal mol^{-1}, for the CH_2OO+H_2O 1b TS and the products with respect to the VDW complex calculated by multireference and single reference methods with aug-cc-pVTZ. Zero-point correction was calculated with B3lYP/6-311+(2d,2p), and the zero of energy is the VDW complex CI…H_2O.

	TS	Prd
QCISD(T)	8.64	-34.94
CCSD(T)	8.39	-35.82
MRCI (10,10)	15.98	-36.60
MRCI+Q Davidson (10,10)	9.79	-35.92

MRCI+Q Pople (10,10)	8.96	-35.80
CASPT2 (10,10)	8.52	-36.10

In Table S4, we compare the complete basis set (CBS) values obtained by CCSD(T) and QCISD(T) using aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ. All in all, the barrier energies are once again within 0.3 kcal mol^{-1} of each other.

Table S4 Zero-point corrected energy, in kcal mol^{-1}, of CH_2OO+H_2O 1a/1b reaction pathway and $CH_2OO+(H_2O)_2$ 2a reaction pathway. Electronic energy difference between QCISD(T) and CCSD(T). Zero-point correction was calculated with B3lYP/6-311+(2d,2p), and the zero of energy is the reactants, $CI+H_2O$ or $CI+(H_2O)_2$.

sCI_2a	VDW	TS	Prd	TS-VDW
QCISD(T)/CBS	-10.83	-6.61	-44.73	4.22
CCSD(T)/CBS	-11.15	-7.17	-46.48	3.98
sCI_1a	VDW	TS	Prd	TS-VDW
QCISD(T)/CBS	-6.52	3.69	-41.30	10.22
CCSD(T)/CBS	-6.62	3.30	-42.31	9.92
sCI_1b	VDW	TS	Prd	TS-VDW
QCISD(T)/CBS	-6.53	2.82	-41.42	9.34
CCSD(T)/CBS	-6.62	2.43	-42.42	9.05

2. Accuracy of the calculated geometries

Next we examine the effect of using the geometries optimized using the B3LYP/6-311+G(2d,2p). In the previous section, we have shown the validity of using the QCISD(T) energies. Therefore, we performed geometry optimization using this method for the CH_2OO + H_2O 1a channel and CH_2OO + $(H_2O)_2$ 2a channel. In Table S5, we compare the geometry optimized with B3LYP/6-311+G(2d,2p) versus those optimized with QCISD(T)/aug-cc-pVTZ. In addition we performed QCISD(T) single point calculation on geometries

optimized with ωB97X-D[6]/6-311++G(3df,3pd). We see that the bond lengths are within 0.01 Angstrom; and the bond angles and the dihedral angles are within 10 degrees of each other. Last, to examine the contribution of this slight geometry difference toward the energetics, we list the errors of the single point energies calculated by QCISD(T)/aug-cc-pVTZ obtained at the B3LYP/6-311+G(2d,2p) and ω B97X-D/6-311++G(3df,3pd) geometries versus those obtained at the QCISD(T)/aug-cc-pVTZ geometries. As seen in Table S6 the error due to the variation in geometries is ~0.3 kcal mol^{-1} for B3LYP. Furthermore, errors due the geometry are both positive for the VDW and TS geometries, thereby the barrier energies, the difference between the TS and VDW, have smaller errors. For example the barrier energy for the 1a (2a) reaction channel is 9.61 (3.60) kcal mol^{-1} at QCISD(T) geometries, while it is 9.47 (3.52) kcal mol^{-1} at B3LYP geometries. Therefore, for the present system B3LYP/6-311+G(2d,2p) geometries can give reasonable estimates. Single point energies obtained by ωB97X-D/6-311++G(3df,3pd) geometries gives slightly larger errors, for the present case. This is because the ωB97X-D gives slightly shorter bond lengths compared to QCISD(T).

Table S5 Geometry parameters optimized by different methods: QCISD(T) /aug-cc-pVTZ (AVTZ), B3LYP /6-311+G(2d,2p), and ωB97X-D/6-311++G(3df,3pd). Units: bond length: Angstrom; angle: degree.

CH_2OO 1a VDW	QCISD(T) /AVTZ	B3LYP /6-311+G(2d,2p)	ωB97X-D /6-311++G(3df,3pd)
RC1O2=	1.270	1.252	1.242
RO2O3=	1.373	1.366	1.345
RC1H4=	1.086	1.086	1.088
RC1H5=	1.082	1.082	1.082
RC1O6=	3.039	3.044	3.040
RO6H7=	0.976	0.977	0.974

RO6H8=	0.961	0.96	0.956
AC1O2O3=	118.6	119.9	119.9
AO2C1H4=	120.2	120.6	120.3
AO2C1H5=	113.7	114.1	114.3
AO2C1O6=	93.5	92.6	92.5
AC1O6H7=	61.5	61.7	60.4
AC1O6H8=	156	155	146.8
DO3O2C1H4=	-0.7	-0.7	0.8
DO3O2C1H5=	179.8	179.9	-179.9
DO3O2C1O6=	-2.7	-2.6	3.0
DO2C1O6H7=	0.2	0.2	-0.4
DO2C1O6H8=	-63	-68.4	74.2

CH_2OO 1a TS	QCISD(T) /AVTZ	B3LYP /6-311+G(2d,2p)	ωB97X-D /6-311++G(3df,3pd)
RC1O2=	1.276	1.272	1.263
RO2O3=	1.465	1.455	1.425
RC1H4=	1.084	1.082	1.084
RC1H5=	1.086	1.084	1.084
RC1O6=	1.962	1.964	1.946
RO6H7=	1.055	1.069	1.051
RO6H8=	0.965	0.963	0.959
AC1O2O3=	105.5	106.4	107.0
AO2C1H4=	118.8	119.1	118.9
AO2C1H5=	115.4	115.3	115.5
AO2C1O6=	94.8	94.9	94.9
AC1O6H7=	77.2	77.4	78.0
AC1O6H8=	112.8	111.7	112.9
DO3O2C1H4=	37.4	39.8	38.7
DO3O2C1H5=	-164.9	-164	-164.9
DO3O2C1O6=	-56	-54	-55.2

DO2C1O6H7=	37.3	36	36.0
DO2C1O6H8=	139.2	139.3	139.3

CH_2OO 2a VDW	QCISD(T) /AVTZ	B3LYP /6-311+G(2d,2p)	ωB97X-D /6-311++G(3df,3pd)
RC1O2=	1.256	1.245	1.236
RO2O3=	1.404	1.401	1.377
RC1H4=	1.083	1.081	1.082
RC1H5=	1.082	1.081	1.081
RO3O6=	2.714	2.705	3.438
RC1O7=	2.578	2.507	2.704
RO6H8=	0.985	0.99	0.987
RO7H9=	0.98	0.985	1.744
RO6H10=	0.961	0.96	2.381
RO7H11=	0.961	0.961	1.542
AC1O2O3=	115.9	116.7	116.9
AO2C1H4=	119.5	120.1	119.8
AO2C1H5=	115.5	115.7	116.0
AO2O3O6=	96.8	97.9	68.3
AO2C1O7=	111.2	108.5	45.8
AO7O6H8=	97.3	94.1	49.0
AC1O7H9=	90.8	93.7	51.1
AO3O6H10=	110.7	111.3	20.2
AO6O7H11=	111.5	109.6	146.4
DO3O2C1H4=	1.9	4	3.5
DO3O2C1H5=	180.2	179.7	179.5
DC1O2O3O6=	72	75.7	-51.8
DO3O2C1O7=	-83	-81.2	-141.1
DO3O7O6H8=	0	-0.3	33.9
DO6C1O7H9=	0.8	1.3	-142.4

DO7O3O6H10=	-127.1	-123.4	-113.1
DC1O6O7H11=	132.9	121.4	101.4

CH_2OO 2a TS	QCISD(T) /AVTZ	B3LYP /6-311+G(2d,2p)	ωB97X-D /6-311++G(3df,3pd)
RC1O2=	1.278	1.274	1.266
RO2O3=	1.467	1.457	1.427
RC1H4=	1.084	1.082	1.084
RC1H5=	1.086	1.083	1.084
RO3O6=	2.509	2.487	2.504
RC1O7=	1.871	1.875	1.856
RO6H8=	1.043	1.066	1.042
RO7H9=	1.04	1.063	1.037
RO6H10=	0.962	0.96	0.956
RO7H11=	0.967	0.965	0.961
AC1O2O3=	110.4	111.9	112.2
AO2C1H4=	117.8	118.2	117.9
AO2C1H5=	114.3	114.1	114.4
AO2O3O6=	95.2	95.7	97.2
AO2C1O7=	109.9	110.2	109.9
AO7O6H8=	87.8	88.4	87.3
AC1O7H9=	101.2	100.5	101.5
AO3O6H10=	110.8	111.7	111.5
AO6O7H11=	104.1	105.8	104.8
DO3O2C1H4=	20.5	22	21.3
DO3O2C1H5=	171	171.2	170.8
DC1O2O3O6=	71.8	69.4	68.2
DO3O2C1O7=	-83	-82	-82.7
DO3O7O6H8=	-0.3	-0.2	-0.7
DO6C1O7H9=	3.5	2.8	3.9

DO7O3O6H10=	-120.2	-118.5	-121.0
DC1O6O7H11=	108.8	108.9	109.4

Table S6 QCISD(T)/aug-cc-pVTZ electronic energy errors, in kcal mol^{-1}, calculated at geometries optimized with B3LYP /6-311+G(2d,2p) and ω B97X-D/6-311++G(3df,3pd). Zero of energy is at the QCISD(T) optimized geometries

	B3LYP/6-311+G(2d.2p)	ωB97X-D/6-311++G(3df,3pd)
CH_2OO 1a VDW	0.28	0.95
CH_2OO 1a TS	0.14	0.61
	B3LYP/6-311+G(2d.2p)	ωB97X-D/6-311++G(3df,3pd)
CH_2OO 2a VDW	0.30	0.84
CH_2OO 2a TS	0.22	0.61

As a conclusion the use of QCISD(T)/CBS energies gives results that are 0.3 kcal mol^{-1} higher than CCSD(T)/CBS. On the other hand, at the aug-cc-pVTZ basis level, QCISD(T) values are 0.3 kcal mol^{-1} lower than those calculated by multireference methods. Use of B3LYP/6-311+G(2d,2p) geometries causes a 0.2 kcal mol^{-1} underestimation compared to the use of QCISD(T)/aug-cc-pVTZ geometries, thereby we estimate the error of our QCISD(T)/CBS//B3LYP/6-311+G(2d,2p) energetics to be 0.5 kcal mol^{-1}.

3. Comparison of the different methods to calculate the rate

In Figure S2 and Table S7, we present the effective rate coefficients for the CH_2OO water vapor reaction at $[H_2O]=5.4\times10^{17}$ cm^{-3} calculated by the 1. rigid rotor harmonic oscillation approximation (RRHO); 2. VPT2 anahrmonic approximation (VPT2) and 3. VPT2 anharmonic corrections with hindered rotor approximation (VPT2+HR). Consistent with the overestimation of the dimer reaction bimolecular rate coefficient, the RRHO gives results that are two timer greater than the VPT2 results. In Figure S3 and Table S8, the comparison of

the rates with different quantum chemistry methods is given. We can see that the use of B3LYP energies or QCISD(T)/aug-cc-pVTZ energies can give rate coefficients that are one order of magnitude greater than the experimental values. In Table S9 we summarize the effective rate coefficients at $[H_2O]=5.4\times10^{17}$ cm^{-3} for all the CI water reaction calculated in the present study.

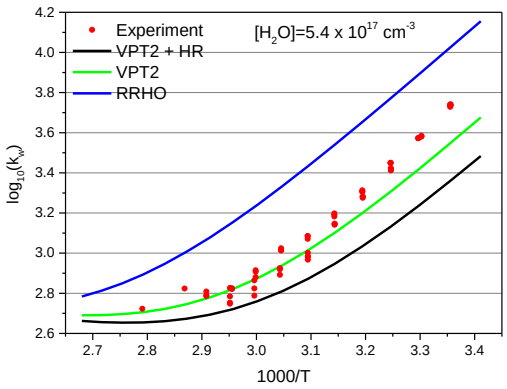


Fig. S2 Effective rate coefficient, in sec^{-1}, for $CH_2OO+(H_2O)_n$, (n=1,2) calculated using: RRHO, VPT2, and VPT2+HR approximations with energetics obtained by QCISD(T)/CBS//B3LYP/6-311+G(2d,2p). Experimental values (this work and Ref. 2) are also give in red dots. $[H_2O]=5.4$ x 10^{17} cm^{-3}

Table S7 Effective rate coefficient, in sec^{-1}, for $CH_2OO+(H_2O)_n$, n=1,2 calculated using: RRHO, VPT2, and VPT2+HR approximations with energetics obtained by QCISD(T)/CBS//B3LYP/6-311+G(2d,2p). $[H_2O]=5.4\times10^{17}$ molecule cm^{-3}

	VPT2+HR		VPT2		RRHO	
T(C)	k_{dimer}	k_{mono}	k_{dimer}	k_{mono}	k_{dimer}	k_{mono}
20	2858	188	4556	188	14153	158
25	2075	199	3304	199	10341	168
30	1521	211	2420	211	7637	178
35	1126	223	1793	223	5693	188
40	843	235	1342	235	4283	199
45	636	247	1014	247	3252	210

50	484	260	773	260	2490	222
55	372	274	595	274	1922	233
60	288	288	462	288	1495	245
65	225	302	361	302	1171	258
70	177	316	285	316	924	270
75	140	331	226	331	734	283
80	112	346	181	346	587	297
85	90	362	146	362	472	310
90	73	378	118	378	382	324
95	59	394	97	394	311	339
100	48	411	79	411	255	353

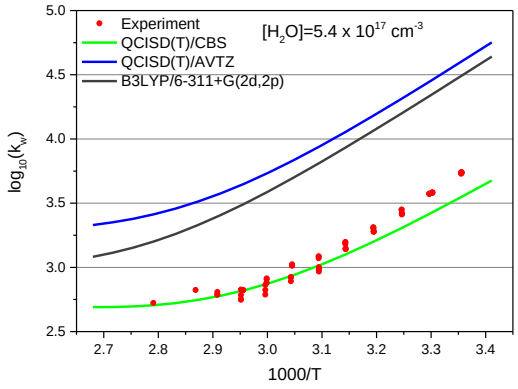


Fig. S3 Effective rate coefficient, in sec^{-1}, for $CH_2OO+(H_2O)_n$, n=1,2 calculated using: QCISD(T)/CBS, QCISD(T)/aug-cc-pVTZ, and B3LYP/6-311+G(2d,2p). Experimental values (this work and Ref. 2) are also give in red dots. $[H_2O]=5.4\times10^{17}$ cm^{-3}

Table S8 Effective rate coefficient, in sec^{-1}, for $CH_2OO+(H_2O)_{n,n=1,2}$ calculated using: QCISD(T)/CBS, QCISD(T)/aug-cc-pVTZ, and B3LYP/6-311+G(2d,2p). $[H_2O]=5.4\times10^{17}$ cm^{-3}

	QCISD(T)/CBS		QCISD(T)/AVTZ		B3LYP/6-311+G(2d,2p)	
T(K)	k_{dimer}	k_{mono}	k_{dimer}	k_{mono}	k_{dimer}	k_{mono}
293	4556	188	55493	1032	43371	403
298	3304	199	38605	1063	30285	421
303	2420	211	27146	1093	21374	440
308	1793	223	19340	1126	15275	459

313	1342	235	13945	1157	11051	479
318	1014	247	10149	1189	8073	499
323	773	260	7470	1221	5956	519
328	595	274	5558	1255	4446	540
333	462	288	4171	1288	3346	561
338	361	302	3156	1321	2539	582
343	285	316	2415	1356	1948	605
348	226	331	1861	1390	1505	627
353	181	346	1444	1425	1171	650
358	146	362	1131	1461	920	673
363	118	378	893	1497	728	697
368	97	394	709	1533	579	721
373	79	411	566	1569	464	745

Table S9 Effective rate constant, in sec^{-1}, by VPT2 scheme for CH_2OO, $CH_3CHOO+(H_2O)_n$, n=1,2. $[H_2O]=5.4\times10^{17}$ cm^{-3}

	CH_2OO		anti CH_3CHOO		syn CH_3CHOO	
T(K)	k_{dimer}	k_{mono}	k_{dimer}	k_{mono}	k_{dimer}	k_{mono}
293	4556	188	14026	19052	20.22	0.09
298	3304	199	9736	18340	15.53	0.11
303	2420	211	6829	17656	12.01	0.12
308	1793	223	4857	17095	9.42	0.15
313	1342	235	3497	16593	7.45	0.17
318	1014	247	2542	16106	5.93	0.19
323	773	260	1868	15689	4.77	0.22
328	595	274	1389	15316	3.87	0.26
333	462	288	1041	14959	3.16	0.29
338	361	302	787	14632	2.59	0.34
343	285	316	602	14364	2.15	0.38
348	226	331	463	14089	1.79	0.43
353	181	346	359	13826	1.50	0.49
358	146	362	281	13610	1.26	0.55
363	118	378	222	13399	1.07	0.62
368	97	394	176	13200	0.91	0.69
373	79	411	141	13008	0.78	0.77

4. Water dimer equilibrium calculation

In Figure S4, we present the equilibrium constant K_{eq} for water dimer, $2H_2O \rightleftharpoons (H_2O)_2$, calculated using several different approximations, along with the literature values reported by Ruscic.[7] We note that the accurate theoretical estimates for K_{eq} in a floppy system such as water dimer requires the complete calculation of accurate vibrational states, and this has been pursued by Leforestier and coworkers,[8,9] as well as by Bowman and coworkers[10]. Since these methods are not applicable to larger systems such as $CI(H_2O)_2$, we compare the validity as well as errors induced by using simpler approximations. For the dimer zero-point-corrected binding energy, we used the QCISD(T)/CBS//B3LYP/6-311+G(2d,2p) value of 2.82 kcal mol^{-1}. First, using the rigid rotor harmonic oscillator (RRHO) approximation, we obtain results (open circles) underestimating Ruscic's[7] values (cross) by an order of magnitude. When anharmonic corrections within the second order vibrational perturbation theory (VPT2)[11] are included we obtain results (open square) that are one third of Rusic's results[7]. It is known that low frequency modes of floppy complexes are more efficiently treated as hindered rotors rather than vibrations. As shown in Fig S5, the two low frequency modes of water dimer can be classified as the out of plane and in plane hindered rotations. Thus using the B3LYP/6-311+G(2d,2p) method, we obtained effective potential energy surfaces along these two rotational coordinates (see Fig S6). When we treat the 2 lowest frequency modes as hindered rotation, while treating the other 10 vibrational modes within the VPT2 approximation we obtain results (filled diamond) within 30% of Ruscic's values. Lastly, if we use the experimental water dimer binding energies of 3.2 kcal/mol reported by Reisler and coworkers[12], we obtain results (open diamonds) which overestimates Ruscic's value. Therefore, we conclude that for the water dimer our approximate treatments are able to estimate the statistical properties to reasonable accuracy if we consider anharmonicity and hindered rotation for the low frequency modes.

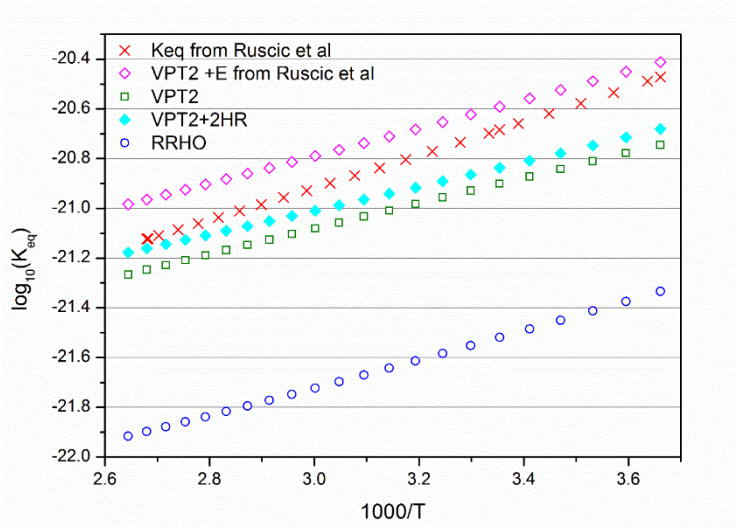


Fig. S4 Arrhenius plot of the equilibrium constant between water and water dimer. The open square represents equilibrium constants calculated with VPT2. The filled diamond represents equilibrium constants calculated with VPT2 plus correction of 2 hindered rotors. The open diamond represents equilibrium constants calculated with VPT2 plus correction by 2 hindered rotors and with the energetics given by Ruscic et al.[7] The open circle represents equilibrium constants calculated with RRHO.

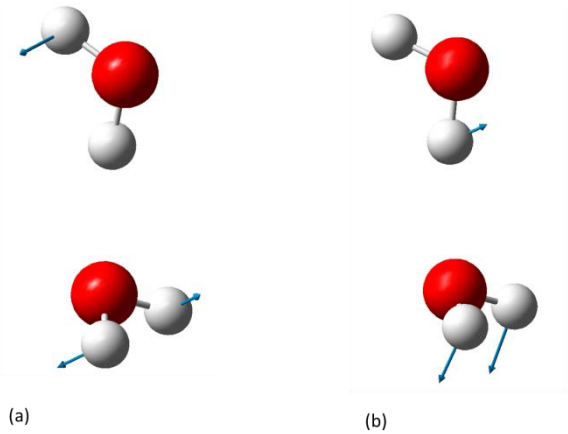


Fig. S5 Two lowest vibrational normal modes of $(H_2O)_2$. (a) This mode has vibrational frequency value at 136.94 cm^{-1} . We substitute this normal mode with out of plane hindered rotation (b) This mode has vibrational frequency value at 159.56 cm^{-1}. We substitute this normal mode with in plane hindered rotation.

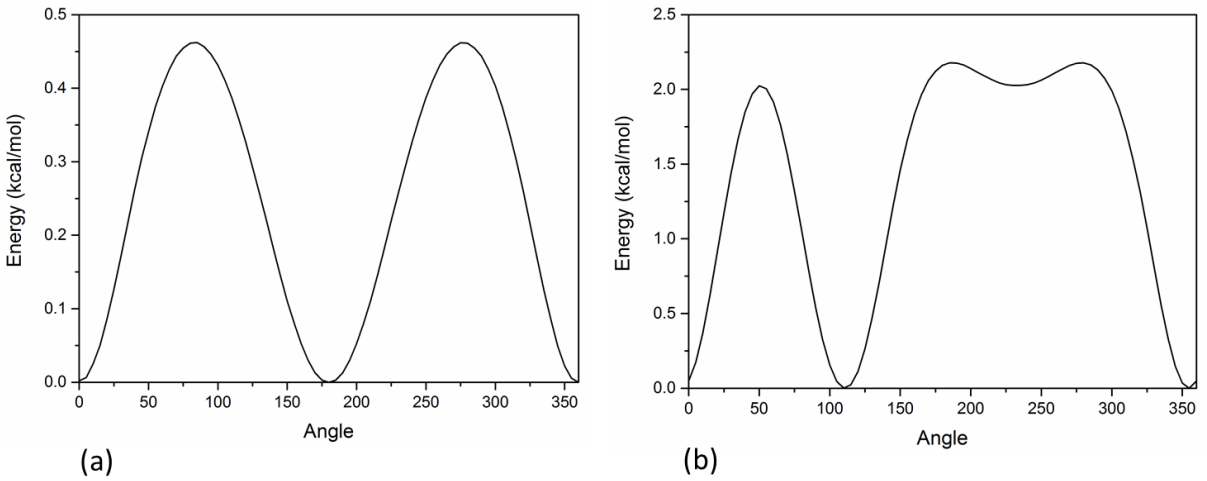


Fig. S6 Effective potential energy surface the (a) out of plane hindered rotation and (b) in plane hindered rotation of water dimer.

5. Hindered rotor approximation model

Since the inclusion of hindered rotor was used for the water dimer calculation, we also considered the effect of hindered rotor approximation for the free OH bonds of the water molecules in the $CH_2OO(H_2O)_2$ complex. In Figure S7, we present the schematic diagram of the TS for the four channels. The previous study by Ariya's group[13–15] located 2a and 2b, but did not consider 2c and 2d. The conformation change from 2a to 2c is due to the rotation of O7H11, and that for 2a to 2d is due to the rotation of O6H10. On the other hand, the conformation change from 2b to 2c is due to the rotation of O6H10, and that for 2b to 2d is due to the rotation of O7H11. Figure S8 we present the potential energy surface (PES) along these rotation angles.

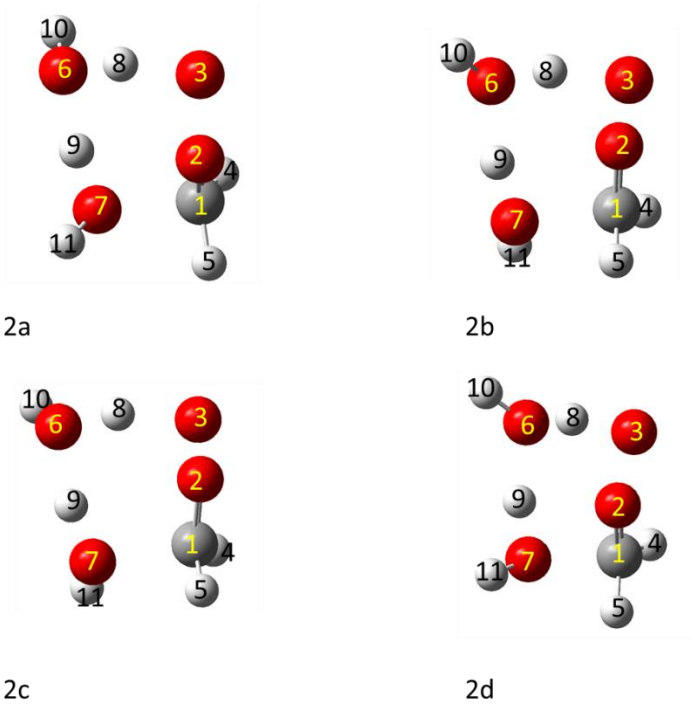


Fig. S7 Schematic geometry for the transition state of $CH_2OO+(H_2O)_2$ geometries 2a, 2b 2c and 2d.

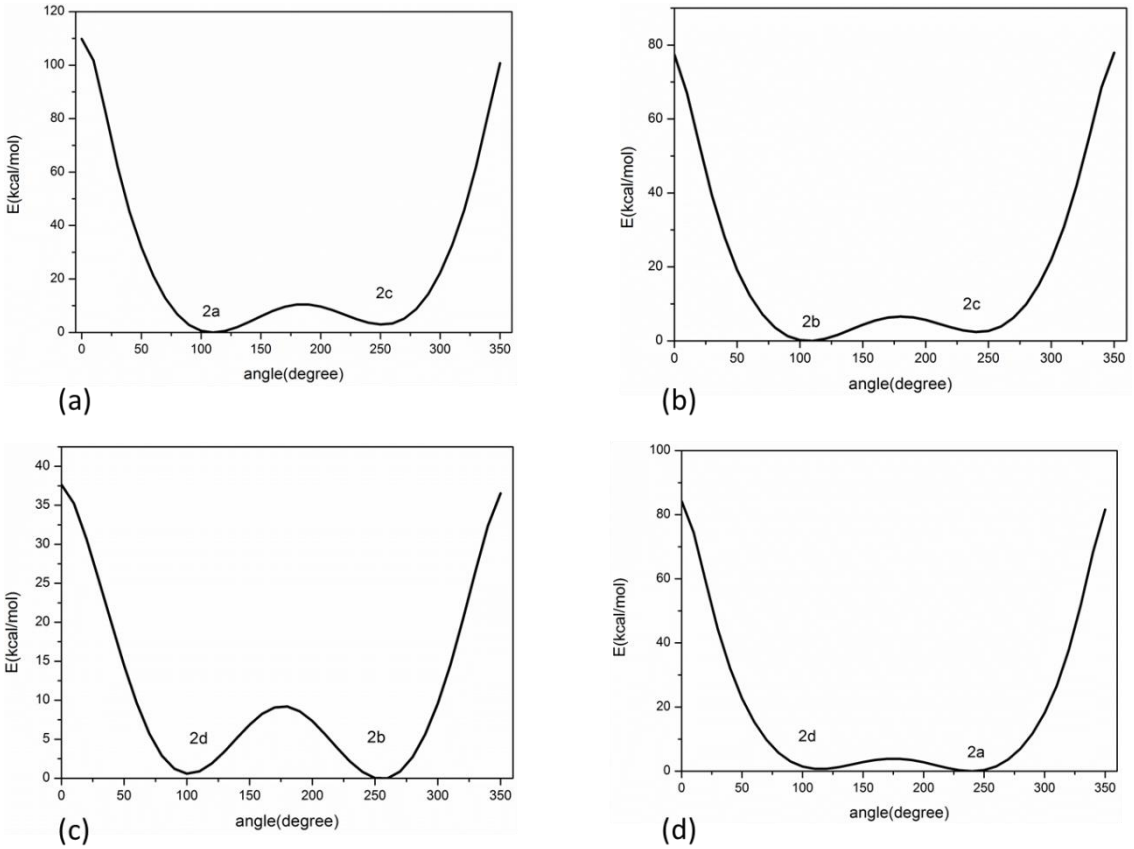


Fig. S8 Potential energy curve by rotating (a) O7H11 and (b) O6H10 from the 2a TS geometry and rotating (c) O6H10 and (d) O7H11 from the 2b TS geometry. The energy is calculated with B3LYP/6-311+G(2d,2p).

We performed 1D hindered rotor approximation using the potential PES given above while removing two vibrational normal modes that corresponds to the hindered rotation. The schematics of these vibrations for 2a TS are given in Figures S9.

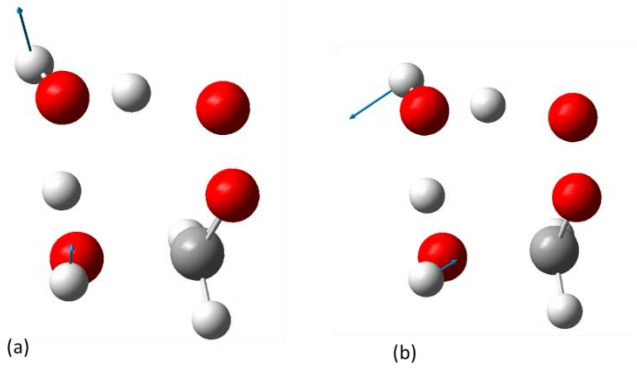


Fig. S9 Normal mode vibrations of 2a TS that were replaced by hindered rotation. (a) The vibrational normal mode (395.71 cm^{-1}) that was substituted with the OH rotation of the water at the OO terminal (Fig S8 (b)). (b) The vibrational normal mode (675.02 cm^{-1}) that was substituted with the OH rotation of water at the carbon terminal (Fig S8 (a)).

6. Variation of the effective rate coefficients due to the errors in the bimolecular rate coefficients

In Figure S10, we present the change of the effective rate coefficients at water concentration [H2O]=1×10^{17} and 2×10^{17} cm^{-3} . Here we used the upper and lower limits of the CI+H_2O and CI+$(H_2O)_2$ reaction given in Figure 7 of the manuscript. We note that we only report the results for the combination for the lowest k_{mono} and highest k_{dimer} as well as highest k_{mono} and lowest k_{dimer}, because use of the combination of the highest k_{mono} and highest k_{dimer} or lowest k_{mono} and lowest k_{dimer} will just cause shifting of the results given in Figure 9 in the manuscript along the Y-axis. As can expected if the larger dimer rates are used it will show a larger negative temperature dependence, while if larger monomer rates are used, it will show small temperature dependence. Here the key point is that even using both limits the effective rates of *anti*-CH_3CHOO are one order greater than CH_2OO. All in all, the effective rates for the CH_2OO, *anti*-CH_3CHOO and *syn*-CH_3CHOO at normal humidity will be ~10^3, ~10^4, and ~10^1 s^{-1}, respectively.

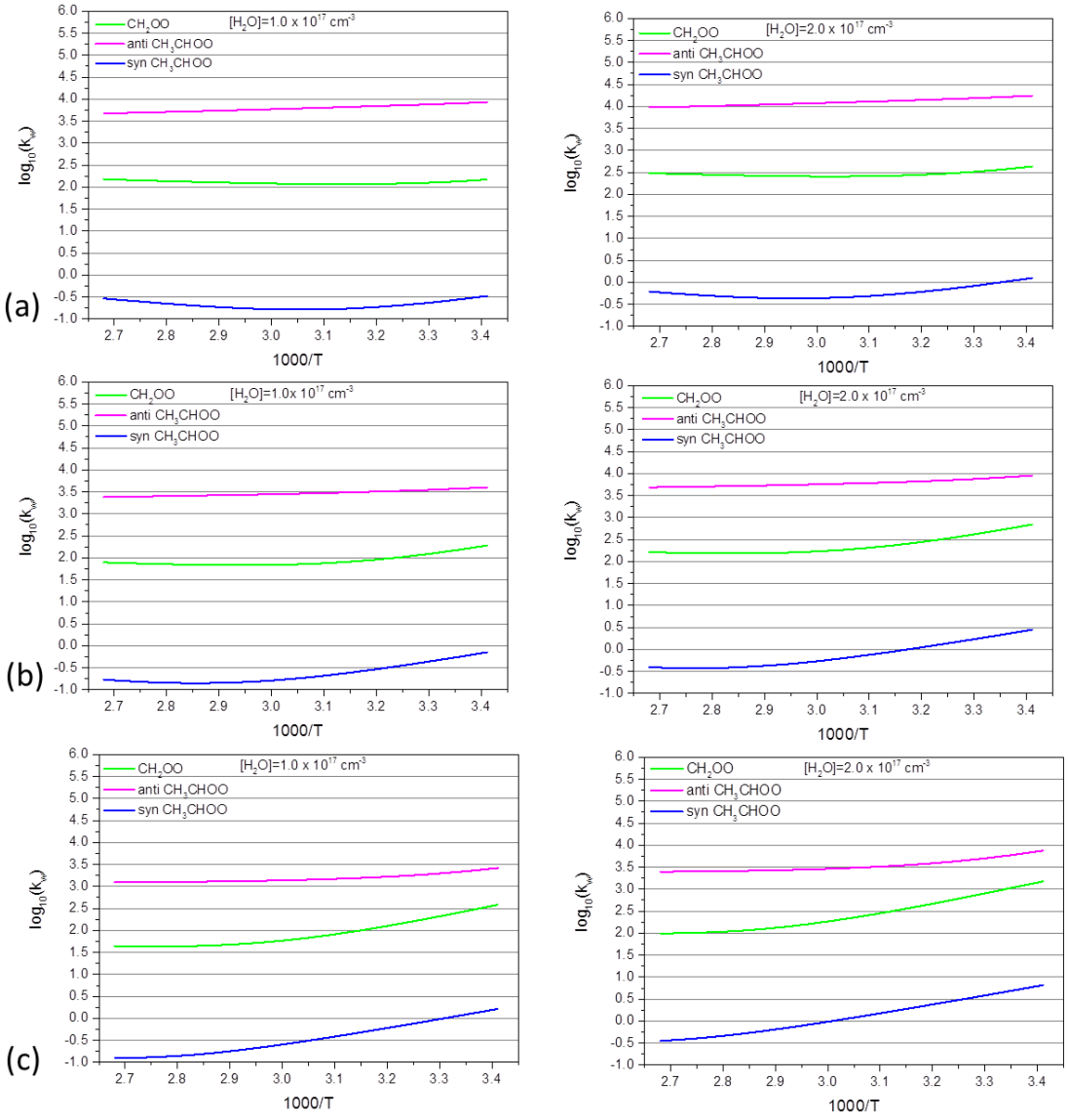
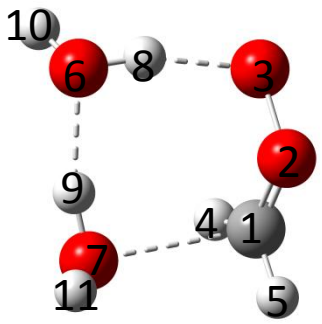
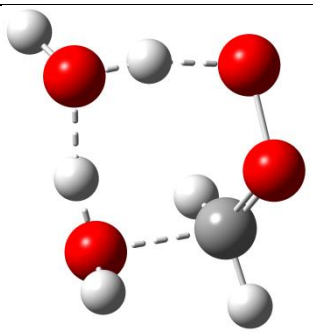
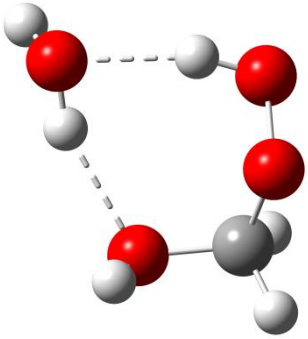


Fig. S10 The Arrhenius plot of the effective rate coefficient, in sec^{-1}, calculated at [H2O]=1×10^{17} (left) and 2×10^{17} cm^{-3} (right) using (a) the highest k_{dimer} and lowest $k_{monomer}$ (b) our best estimates for k_{dimer} and $k_{monomer}$; and (c) the lowest k_{dimer} and highest $k_{monomer}$.

7. *Schematic Figures of the VDW complex, TS, and products for CI+H_2O/$(H_2O)_2$*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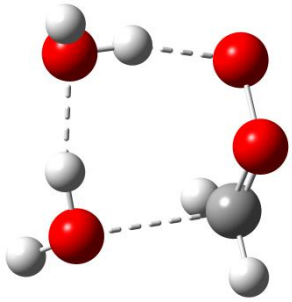	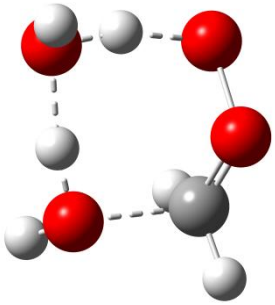	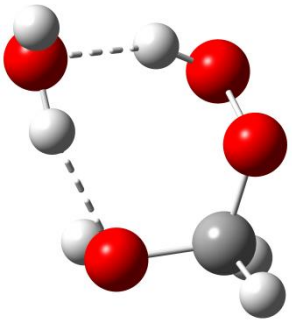
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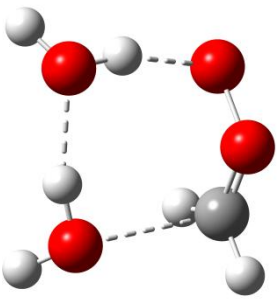	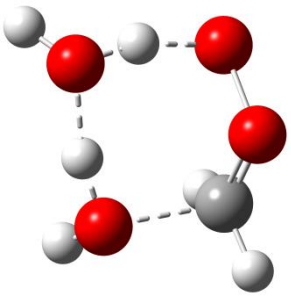	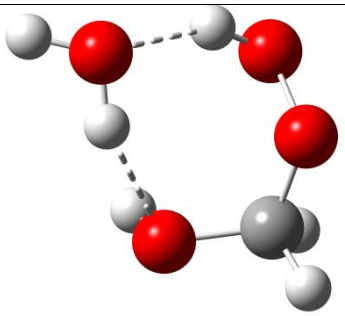
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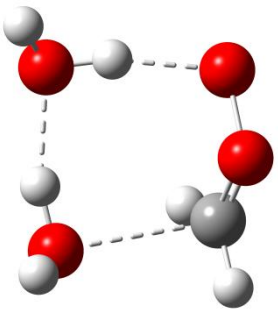
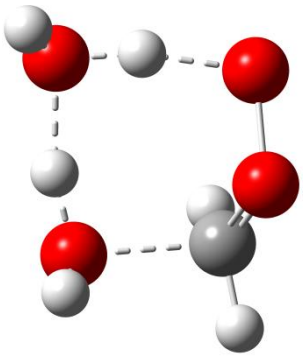
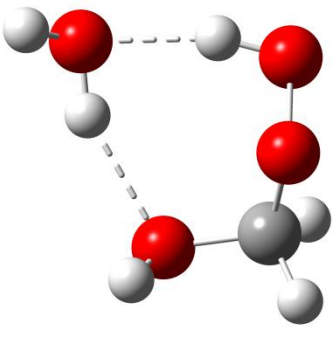
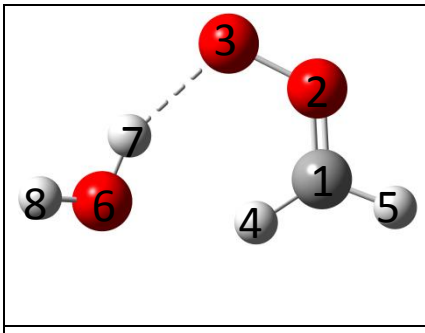
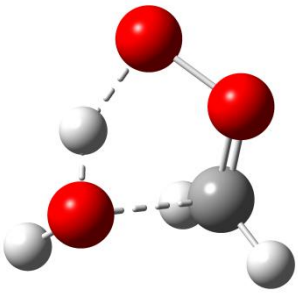
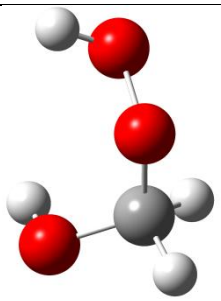
		
CH_2OO 2d VDW	CH_2OO 2d TS	CH_2OO 2d Prd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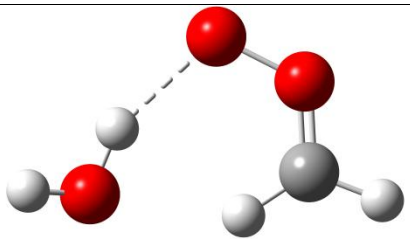	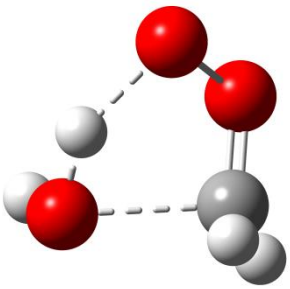	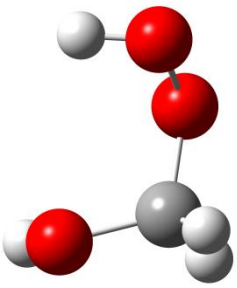
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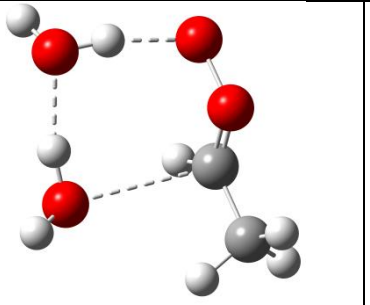	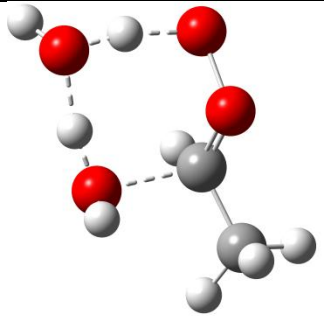	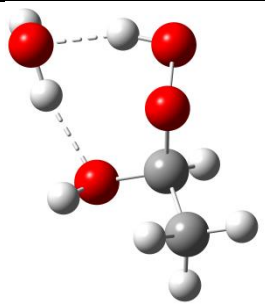
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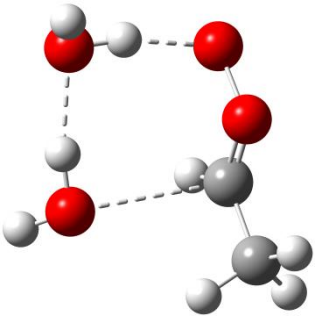	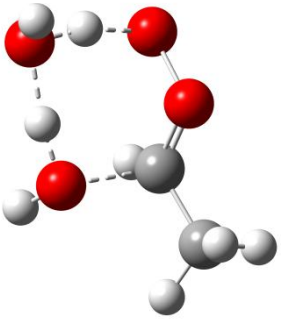	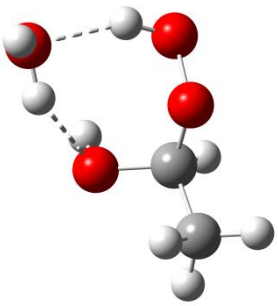
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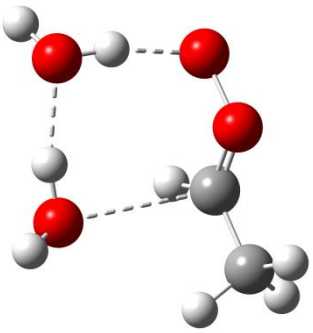	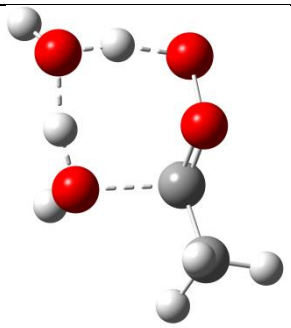	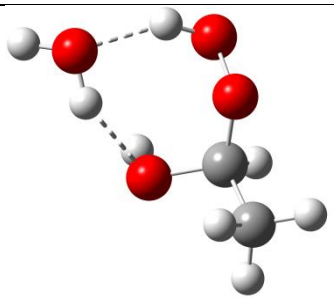
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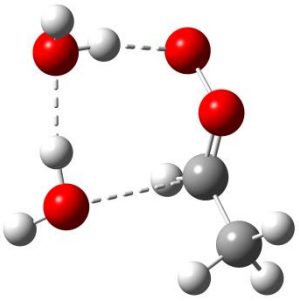
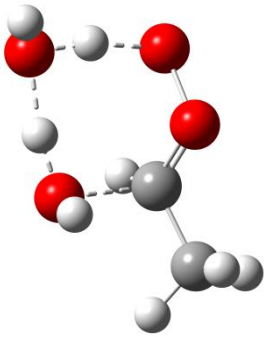
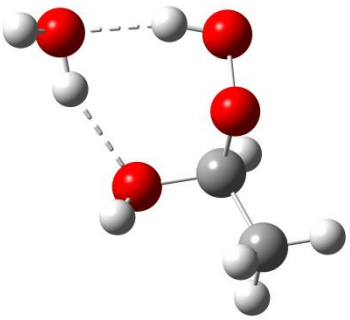
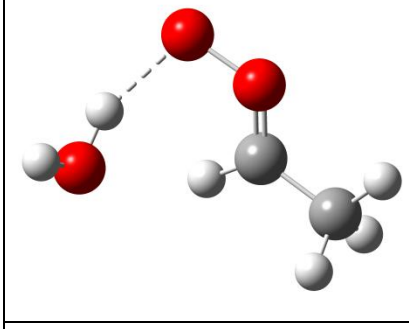
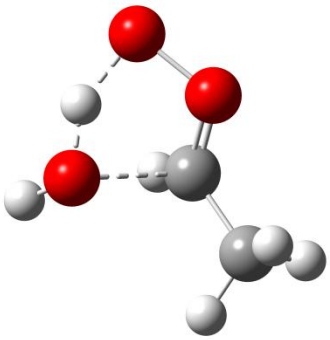
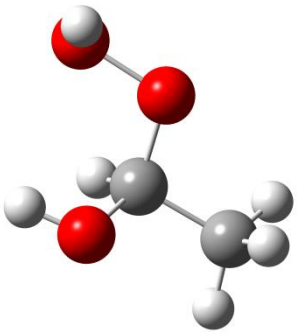
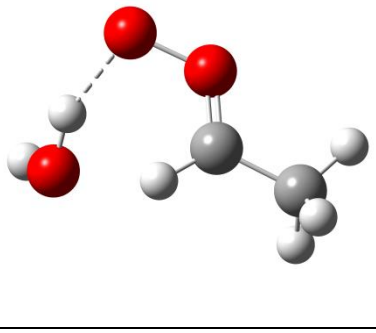
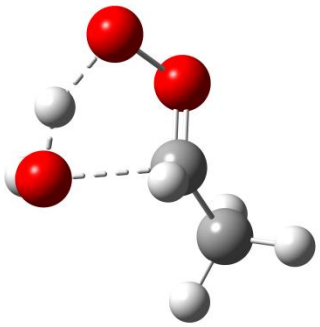
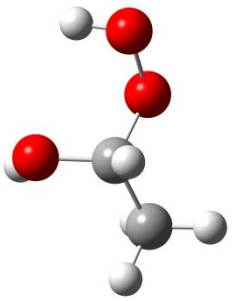
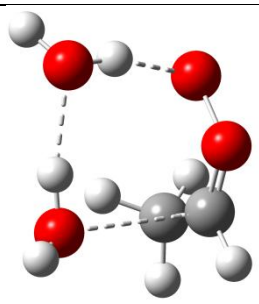
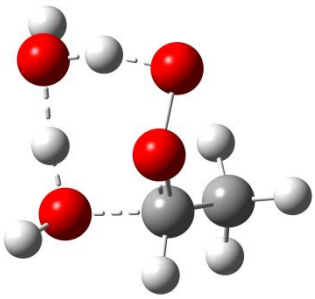
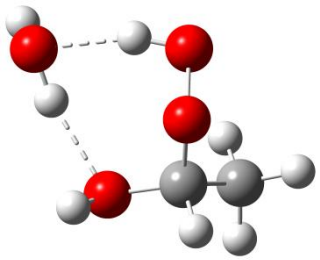
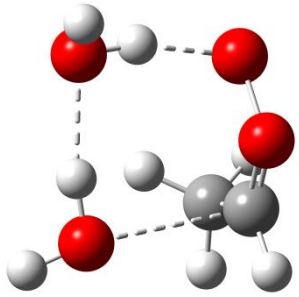
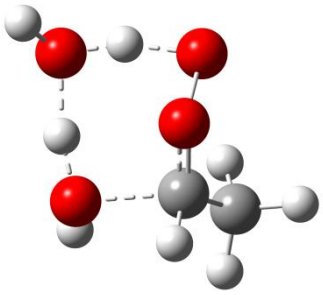
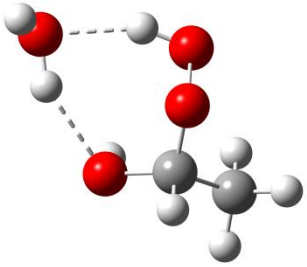
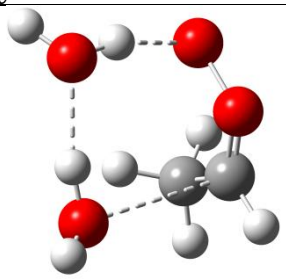
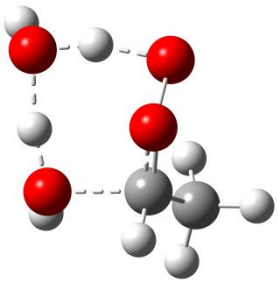
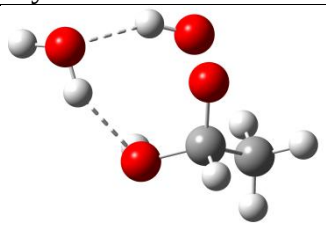
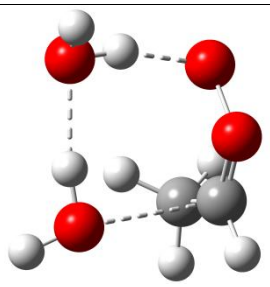
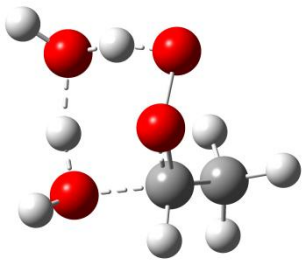
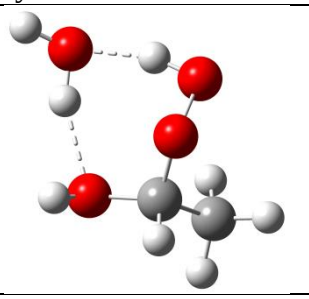
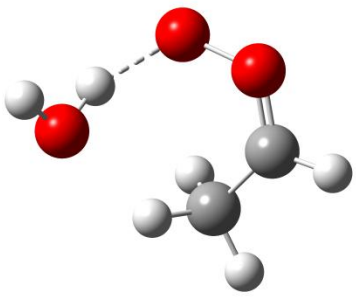
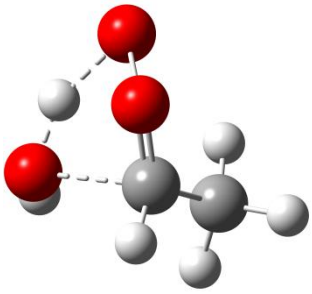
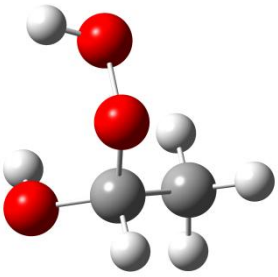
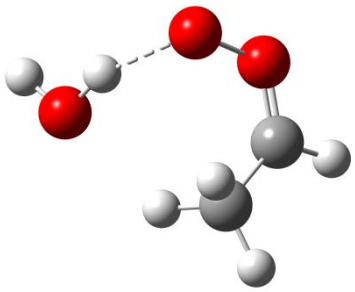
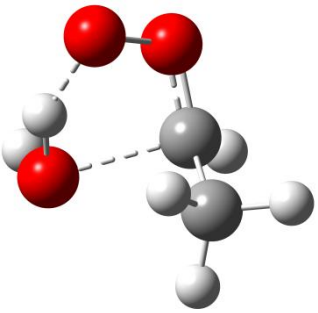
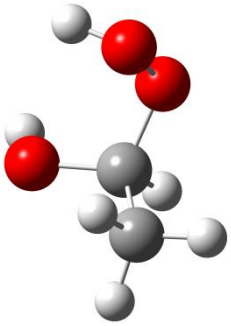
		
anti CH_3CHOO 2d VDW	anti CH_3CHOO 2d TS	anti CH_3CHOO 2d Prd

		
anti CH_3CHOO 1a VDW	anti CH_3CHOO 1a TS	anti CH_3CHOO 1a Prd
		
anti CH_3CHOO 1b VDW	anti CH_3CHOO 1b TS	anti CH_3CHOO 1b Prd

		
syn CH_3CHOO 2a VDW	syn CH_3CHOO 2a TS	syn CH_3CHOO 2a Prd
		
syn CH_3CHOO 2b VDW	syn CH_3CHOO 2b TS	syn CH_3CHOO 2b Prd
		
syn CH_3CHOO 2c VDW	syn CH_3CHOO 2c TS	syn CH_3CHOO 2c Prd
		
syn CH_3CHOO 2d VDW	syn CH_3CHOO 2d TS	syn CH_3CHOO 2d Prd

		
syn CH_3CHOO 1a VDW	syn CH_3CHOO 1a TS	syn CH_3CHOO 1a Prd
		
syn CH_3CHOO 1b VDW	syn CH_3CHOO 1b TS	syn CH_3CHOO 1b Prd

8. Optimized Cartesian geometries obtained by B3LYP/6-311+G(2d,2p)

CH_2OO 2a VDW

C	-0.091096	-0.87165	1.237793
H	0.393534	-1.59205	0.594352
H	-0.923761	-1.10351	1.886429
O	0.357571	0.286347	1.328222
O	1.441911	0.608367	0.501656
O	-1.615941	-0.98289	-0.7485
H	-2.506055	-0.62216	-0.71658
H	-1.086345	-0.33805	-1.27188
O	0.078798	0.862028	-1.82152
H	0.673469	0.879159	-1.03052
H	0.640953	0.675458	-2.57713

CH_2OO 2a Ts

C	1.294993	-0.2905	-0.25319
H	1.96477	-0.99602	-0.72666
H	0.543331	-0.64345	0.442573
O	1.735022	0.87749	0.004484
O	2.879484	1.221819	-0.82817

O	0.172667	-0.24179	-1.75399
H	-0.623048	0.240474	-1.49919
H	0.72238	0.412767	-2.38524
O	1.598645	1.392684	-2.9535
H	2.236305	1.417098	-2.1
H	2.121469	1.107805	-3.70688

CH_2OO 2a Prd

C	-0.400247	-0.94956	0.933539
H	0.375384	-1.69594	0.784754
H	-1.032411	-1.19149	1.789923
O	0.16096	0.28598	1.259185
O	1.353418	0.481594	0.45708
O	-1.169042	-0.92984	-0.26471
H	-1.978901	-0.43687	-0.09498
H	-0.398221	0.160199	-1.71062
O	0.055834	0.966314	-2.00502
H	0.989726	0.878648	-0.36123
H	0.530398	0.7342	-2.80742

CH_2OO 2b VDW

C	-0.574083	-0.74816	1.22943
H	-0.107914	-1.63283	0.818573
H	-1.579371	-0.71362	1.623926
O	0.083387	0.303303	1.332552
O	1.387281	0.280553	0.817404
O	0.718406	0.656029	-1.771
H	0.770946	1.581909	-2.01987
H	1.099079	0.594229	-0.8597
O	-1.616962	-0.55744	-1.04967
H	-0.850279	-0.0794	-1.44175
H	-1.810951	-1.27826	-1.65478

CH_2OO 2b Ts

C	1.935325	-1.38591	-0.67581
H	2.44442	-2.32781	-0.8391
H	0.962635	-1.35741	-0.20215
O	2.654305	-0.36134	-0.44111
O	4.001268	-0.52591	-0.97748
O	3.278765	-0.04105	-3.29354
H	3.213093	0.899818	-3.47471

H	3.72167	-0.16344	-2.32906
O	1.278758	-1.21351	-2.42684
H	2.070489	-0.66881	-2.89615
H	1.242732	-2.07427	-2.86052

CH_2OO 2b Prd

C	-0.935453	-0.58329	0.893509
H	-0.616637	-1.5114	1.369614
H	-1.841819	-0.19195	1.352778
O	0.011204	0.423254	1.11264
O	1.299053	-0.09091	0.680861
O	0.682726	0.927085	-1.86628
H	0.63664	1.875747	-2.01208
H	1.360154	0.327436	-0.20292
O	-1.209515	-0.80007	-0.47933
H	-0.203975	0.653752	-1.58571
H	-0.630287	-1.49886	-0.79823

CH_2OO 2c VDW

C	-0.108059	-0.85607	1.312632
H	0.441547	-1.64163	0.813456
H	-0.996618	-1.01279	1.907306
O	0.31299	0.313824	1.269333
O	1.454496	0.541081	0.491472
O	-1.592164	-0.98556	-0.73304
H	-1.74165	-1.72333	-1.32962
H	-1.100362	-0.31201	-1.25308
O	0.026436	0.979859	-1.77585
H	0.663184	0.939642	-1.02164
H	0.554014	0.959145	-2.5772

CH_2OO 2c Ts

C	1.248183	-0.29301	-0.2257
H	1.912664	-1.09786	-0.51618
H	0.419831	-0.48042	0.445481
O	1.754895	0.870727	-0.10205
O	2.94803	1.013499	-0.92942
O	0.233336	-0.29864	-1.78332
H	0.330522	-1.14648	-2.23195
H	0.73574	0.437778	-2.3835
O	1.538173	1.476232	-2.90496
H	2.265786	1.383025	-2.12114

H	1.977068	1.319411	-3.74423

CH_2OO 2c Prd

C	-0.546551	-0.80246	1.035126
H	0.068093	-1.62421	1.405612
H	-1.401618	-0.62202	1.684279
O	0.169008	0.397998	1.083398
O	1.41246	0.189108	0.361024
O	-1.045368	-1.10391	-0.25629
H	-0.378079	-1.62088	-0.71732
H	-0.720686	0.616036	-1.46346
O	-0.044113	1.209462	-1.82158
H	1.199668	0.652979	-0.47301
H	-0.064158	1.104464	-2.77584

CH_2OO 2d VDW

C	-0.520648	-0.78795	1.140993
H	-0.087951	-1.56652	0.528423
H	-1.487993	-0.86174	1.616537
O	0.136194	0.236243	1.407483
O	1.397213	0.353788	0.80988
O	0.737107	0.508916	-1.79864
H	0.937167	1.370903	-2.17044
H	1.092699	0.515871	-0.87421
O	-1.693981	-0.48108	-1.0498
H	-0.910072	-0.06956	-1.47919
H	-2.406623	0.157779	-1.13422

CH_2OO 2d Ts

C	1.974502	-1.41084	-0.68654
H	2.536101	-2.2587	-1.05652
H	1.044651	-1.5708	-0.15443
O	2.620934	-0.37907	-0.30693
O	3.95682	-0.32895	-0.88642
O	3.294254	-0.16567	-3.26984
H	3.338943	0.72803	-3.61772
H	3.681661	-0.15693	-2.27419
O	1.188895	-1.10122	-2.35783
H	2.009043	-0.66127	-2.87093
H	0.537988	-0.40214	-2.22552

CH_2OO 2d Prd

C	-0.818636	-0.73864	0.831111

H	-0.240337	-1.65805	0.844614
H	-1.6365	-0.76603	1.553182
O	-0.029487	0.339786	1.234258
O	1.316794	0.149168	0.72942
O	0.802722	0.672184	-1.96524
H	0.544004	1.508467	-2.36059
H	1.257631	0.527704	-0.17306
O	-1.332472	-0.60615	-0.49272
H	-0.01952	0.199946	-1.75672
H	-2.055304	0.028909	-0.4713

CH_2OO 1a VDW

C	1.136434	-0.78569	0.23067
H	1.301468	0.246282	-0.06362
H	1.912783	-1.51876	0.403219
O	-0.025899	-1.22495	0.387611
O	-1.09809	-0.39889	0.201331
O	0.135027	1.961041	-0.6169
H	-0.525393	1.278026	-0.38873
H	-0.297702	2.586484	-1.20194

CH_2OO 1a Ts

C	1.046371	0.241018	0.03858
H	1.115162	0.73337	0.999994
H	1.937044	0.010056	-0.53497
O	0.032696	-0.48513	-0.21446
O	-1.119312	0.207552	0.342727
O	0.297599	1.865554	-0.77332
H	-0.562966	1.405913	-0.33581
H	0.492283	2.648366	-0.24669

CH_2OO 1a Prd

C	0.893387	0.066596	0.06636
H	1.037459	0.244041	1.134234
H	1.775154	-0.39382	-0.37638
O	-0.10165	-0.9183	-0.10725
O	-1.267024	-0.46684	0.641306
O	0.641736	1.256193	-0.62299
H	-1.902288	-0.35761	-0.07842
H	0.032067	1.788495	-0.10399

CH_2OO 1b VDW

C	-0.285867	1.359856	0.186721

H	0.755224	1.05955	0.255383
H	-0.650808	2.374704	0.26913
O	-1.182255	0.508725	-0.01495
O	-0.853923	-0.81189	-0.13673
O	1.924818	-0.72635	0.039279
H	1.001147	-1.02364	-0.07517
H	2.484978	-1.37607	-0.39055

CH_2OO 1b Ts

C	0.057513	0.997065	0.246257
H	0.191353	0.821253	1.304934
H	0.411461	1.91553	-0.21062
O	-0.881729	0.404678	-0.37693
O	-0.95162	-0.94194	0.168882
O	1.439398	-0.38356	-0.00564
H	0.544136	-0.95297	0.07696
H	1.68962	-0.40977	-0.93671

CH_2OO 1b Prd

C	0.39098	0.761099	0.255178
H	0.242011	0.727245	1.331713
H	0.491463	1.789029	-0.10214
O	-0.760727	0.302446	-0.41122
O	-1.18533	-0.92729	0.22778
O	1.530106	-0.01428	-0.01636
H	-0.600171	-1.57625	-0.18856
H	1.803825	0.140765	-0.92597

anti-CH_3CHOO 2a VDW

C	0.084709	-0.6937	1.020856
H	0.546204	-1.37127	0.31131
O	0.532442	0.470944	1.080507
O	1.597043	0.790606	0.220082
O	-1.395875	-0.86478	-1.33295
H	-2.285969	-0.72131	-1.66255
H	-0.846298	-0.16044	-1.74288
O	0.299569	1.139291	-2.11752
H	0.842336	1.115451	-1.28835
H	0.917177	1.00182	-2.83972
C	-1.009751	-1.09392	1.922939

H	-1.828936	-1.48183	1.316682
H	-0.668086	-1.906	2.57018
H	-1.349286	-0.25868	2.529114

anti-CH_3CHOO 2a Ts

C	1.231608	-0.28662	-0.23995
H	1.933921	-0.97389	-0.69573
O	1.664152	0.904602	-0.02921
O	2.833335	1.215711	-0.84367
O	0.202363	-0.26148	-1.81746
H	-0.624173	0.191454	-1.61234
H	0.772871	0.425071	-2.43359
O	1.612875	1.390409	-2.95851
H	2.247159	1.402798	-2.05702
H	2.14583	1.097996	-3.70181
C	0.24127	-0.79492	0.756057
H	-0.289735	-1.65611	0.360171
H	0.786788	-1.10123	1.650394
H	-0.462436	-0.0145	1.039681

anti-CH_3CHOO 2a Prd

C	-0.211441	-0.7751	0.618087
H	0.597614	-1.48226	0.448282
O	0.331746	0.476283	0.957789
O	1.526176	0.702072	0.170474
O	-0.923179	-0.72813	-0.62186
H	-1.748313	-0.25162	-0.47251
H	-0.151721	0.376932	-2.02539
O	0.281857	1.194013	-2.32297
H	1.166145	1.104192	-0.64649
H	0.790185	0.963356	-3.10482
C	-1.112234	-1.17683	1.770065
H	-1.59477	-2.12545	1.543546
H	-0.531773	-1.27855	2.684318
H	-1.879633	-0.41842	1.935346

anti-CH_3CHOO 2b VDW

C	-0.33531	-0.56434	1.067984
H	0.107311	-1.44475	0.616142
O	0.369244	0.465849	1.122142
O	1.666233	0.377527	0.581288
O	1.083223	0.745614	-2.01306
H	1.118269	1.679155	-2.23419

H	1.406259	0.67289	-1.07802
O	-1.251885	-0.61246	-1.56884
H	-0.471863	-0.08681	-1.85464
H	-1.394339	-1.25712	-2.26589
C	-1.702128	-0.5335	1.616931
H	-2.395828	-0.72986	0.797012
H	-1.822173	-1.33217	2.352286
H	-1.92479	0.428355	2.070437

anti-CH_3CHOO 2b Ts

C	1.873488	-1.35262	-0.6781
H	2.420948	-2.27558	-0.83258
O	2.594675	-0.30933	-0.48216
O	3.952005	-0.49092	-0.9884
O	3.310704	-0.08339	-3.3039
H	3.232274	0.850567	-3.51298
H	3.721495	-0.18511	-2.28242
O	1.302268	-1.21923	-2.47886
H	2.13125	-0.68128	-2.9424
H	1.273044	-2.08967	-2.89225
C	0.557381	-1.36308	0.022959
H	-0.096952	-2.12004	-0.4005
H	0.732268	-1.5981	1.074775
H	0.081414	-0.38844	-0.04662

anti-CH_3CHOO 2b Prd

C	-0.555003	-0.65436	0.668069
H	-0.130439	-1.5546	1.117365
O	0.326927	0.423243	0.89706
O	1.637082	0.028291	0.414844
O	0.888777	1.106271	-2.07443
H	0.732536	2.050311	-2.16194
H	1.648799	0.495502	-0.4458
O	-0.754364	-0.87817	-0.72301
H	0.046966	0.718555	-1.78929
H	-0.047362	-1.45176	-1.03533
C	-1.872323	-0.25836	1.295842
H	-2.587335	-1.06946	1.176802
H	-1.737808	-0.04958	2.354843
H	-2.265616	0.630739	0.804977

anti-CH_3CHOO 2c VDW

C	0.076248	-0.62071	1.041304
H	0.656264	-1.26169	0.386844

O	0.389028	0.587703	1.089931
O	1.468367	1.001116	0.29007
O	-1.218957	-1.02997	-1.39633
H	-2.095136	-0.99058	-1.78655
H	-0.719041	-0.28373	-1.79533
O	0.30817	1.120194	-2.14082
H	0.791206	1.184887	-1.27756
H	0.985846	1.029688	-2.81497
C	-1.027978	-1.11538	1.882551
H	-1.758073	-1.60354	1.236163
H	-0.646913	-1.87033	2.575303
H	-1.494811	-0.3075	2.43911

anti-CH_3CHOO 2c Ts

C	1.273633	-0.36747	-0.2293
H	1.987968	-1.10419	-0.57979
O	1.730283	0.825868	-0.09992
O	2.911461	1.039923	-0.92855
O	0.285371	-0.3476	-1.83258
H	0.416624	-1.17521	-2.30846
H	0.777965	0.442925	-2.41052
O	1.517406	1.496467	-2.87326
H	2.258126	1.391706	-2.05086
H	1.964278	1.359257	-3.7117
C	0.211752	-0.75156	0.745354
H	-0.306127	-1.64787	0.41529
H	0.686327	-0.95348	1.707604
H	-0.502166	0.058982	0.866543

anti-CH_3CHOO 2c Prd

C	-0.177593	-0.82253	0.697382
H	0.550195	-1.59379	0.959983
O	0.434974	0.44149	0.828921
O	1.639692	0.430938	0.019077
O	-0.630868	-1.0479	-0.63262
H	0.124002	-1.3558	-1.14412
H	-0.609954	0.802473	-1.64481
O	-0.045056	1.521901	-1.96469
H	1.335012	0.967271	-0.7391
H	-0.109963	1.515814	-2.9227
C	-1.36898	-0.80835	1.627654
H	-1.867162	-1.77474	1.591338

H	-1.047996	-0.60737	2.647312
H	-2.072378	-0.03695	1.317681

anti-CH_3CHOO 2d VDW

C	-0.340506	-0.58522	1.047396
H	0.063693	-1.47223	0.573032
O	0.401919	0.417365	1.111622
O	1.688078	0.292233	0.55193
O	1.087201	0.728035	-2.02883
H	1.149104	1.664737	-2.22986
H	1.418973	0.624839	-1.09983
O	-1.290557	-0.55168	-1.5778
H	-0.494249	-0.05262	-1.86642
H	-1.471729	-1.17495	-2.28525
C	-1.698171	-0.51536	1.615224
H	-2.409163	-0.67043	0.801338
H	-1.837781	-1.32317	2.337017
H	-1.879605	0.445007	2.0898

anti-CH_3CHOO 2d Ts

C	1.84741	-1.26802	-0.69295
H	2.422757	-2.14543	-0.9629
O	2.525904	-0.2141	-0.40785
O	3.893048	-0.28594	-0.91318
O	3.371243	-0.25273	-3.29884
H	3.424804	0.622511	-3.68957
H	3.70339	-0.19342	-2.24762
O	1.224501	-1.09748	-2.46215
H	2.103521	-0.69427	-2.95191
H	0.566498	-0.39283	-2.45112
C	0.564822	-1.42814	0.055548
H	-0.07769	-2.15053	-0.43987
H	0.800867	-1.79663	1.055445
H	0.050846	-0.47425	0.159491

anti-CH_3CHOO 2d Prd

C	-0.563454	-0.60349	0.565697
H	0.045128	-1.50219	0.632395
O	0.212589	0.504205	0.950096
O	1.581763	0.29439	0.526508
O	1.233632	0.686889	-2.21934
H	0.982727	1.502813	-2.65962
H	1.572413	0.629262	-0.39459
O	-0.958198	-0.52493	-0.80944

H	0.407139	0.21772	-2.01696
H	-1.688405	0.101091	-0.87112
C	-1.764647	-0.63452	1.490684
H	-2.425086	-1.45227	1.208947
H	-1.442339	-0.77229	2.520284
H	-2.316338	0.305698	1.429771

anti-CH_3CHOO 1a VDW

C	0.761602	-0.40816	0.200601
H	0.800459	0.494067	0.80149
O	-0.363411	-0.90664	-0.03032
O	-1.48166	-0.25948	0.487064
O	-0.539869	2.199801	-0.25379
H	-1.101808	1.44396	0.023825
H	-1.056613	2.692273	-0.89508
C	1.9602	-1.05604	-0.36623
H	2.477425	-0.34559	-1.01629
H	2.656098	-1.31353	0.435891
H	1.69921	-1.94736	-0.93025

anti-CH_3CHOO 1a Ts

C	1.060914	0.213194	-0.02917
H	1.108858	0.628898	0.970643
O	0.007888	-0.45169	-0.33301
O	-1.120789	0.242181	0.271327
O	0.306986	1.930134	-0.68321
H	-0.569304	1.40399	-0.26013
H	0.510264	2.658702	-0.08745
C	2.302566	-0.08503	-0.7826
H	2.934353	0.800158	-0.8109
H	2.852042	-0.87428	-0.26341
H	2.07401	-0.40822	-1.79419

anti-CH_3CHOO 1a Prd

C	0.522025	0.136147	0.181767
H	0.641891	0.243479	1.263392
O	-0.51771	-0.8103	-0.04253
O	-1.679319	-0.33507	0.694945
O	0.239215	1.381303	-0.40087
H	-2.301529	-0.20344	-0.0322
H	-0.439704	1.810782	0.128285
C	1.750394	-0.45104	-0.47574
H	2.596451	0.211463	-0.3059

H	1.972919	-1.43106	-0.05971
H	1.58672	-0.54287	-1.54821

anti-CH_3CHOO 1b VDW

C	-0.137834	0.85913	0.173483
H	0.387549	0.511182	1.056375
O	-0.879849	0.04507	-0.42182
O	-0.964906	-1.24895	0.082848
O	1.737588	-1.39853	0.467945
H	0.784174	-1.59914	0.344406
H	2.215164	-2.06528	-0.0302
C	-0.00281	2.227244	-0.36268
H	-0.284296	2.954427	0.402759
H	1.046607	2.414568	-0.60468
H	-0.614957	2.367402	-1.24942

anti-CH_3CHOO 1b Ts

C	0.033084	1.016217	0.138107
H	0.019534	0.866474	1.210714
O	-0.800665	0.338438	-0.56336
O	-0.88186	-0.98408	0.041737
O	1.451913	-0.37273	0.169055
H	0.512346	-0.94837	0.153562
H	1.833166	-0.45752	-0.7124
C	0.53661	2.291758	-0.4282
H	-0.107916	3.106287	-0.08867
H	1.538876	2.484526	-0.05062
H	0.540097	2.270248	-1.51495

anti-CH_3CHOO 1b Prd

C	0.234527	0.404388	0.304745
H	-0.05234	0.413499	1.355147
O	-0.822032	-0.15571	-0.45496
O	-1.249321	-1.37247	0.200936
O	1.386934	-0.40985	0.244095
H	-0.522781	-1.97578	-0.01515
H	1.780566	-0.32102	-0.63129
C	0.449232	1.797533	-0.25407
H	-0.451929	2.396907	-0.14231
H	1.266117	2.277923	0.280757
H	0.700593	1.748637	-1.31489

syn-CH_3CHOO 2a VDW

C	-0.035608	-0.67094	1.282648

H	-0.896015	-0.7852	1.930944
O	0.303089	0.529064	1.14219
O	1.386244	0.779366	0.295943
O	-1.814007	-0.65429	-0.97847
H	-2.746044	-0.49477	-1.14289
H	-1.341477	0.104307	-1.38015
O	-0.214313	1.465424	-1.8074
H	0.464717	1.34464	-1.10206
H	0.262857	1.461309	-2.64031
C	0.677207	-1.78984	0.660057
H	1.744542	-1.69442	0.871452
H	0.281684	-2.74081	1.003495
H	0.570449	-1.71208	-0.42397

syn-CH_3CHOO 2a Ts

C	1.361606	-0.31734	-0.34619
H	0.597118	-0.59123	0.374121
O	1.775122	0.885121	-0.12072
O	2.901346	1.277269	-0.95609
O	0.190928	-0.23042	-1.81142
H	-0.606435	0.21235	-1.498
H	0.714141	0.507016	-2.42459
O	1.498301	1.508352	-2.94071
H	2.225844	1.498273	-2.09694
H	1.957358	1.297293	-3.75689
C	2.262978	-1.3953	-0.84455
H	3.044146	-1.53686	-0.09485
H	1.703664	-2.31783	-0.97038
H	2.745995	-1.11228	-1.77255

syn-CH_3CHOO 2a Prd

C	-0.42194	-0.73646	0.801397
H	-1.055624	-0.95432	1.665682
O	0.133109	0.50501	1.178266
O	1.24496	0.851041	0.313985
O	-1.242239	-0.61768	-0.36424
H	-2.002207	-0.07204	-0.13401
H	-0.585653	0.576215	-1.78878
O	-0.235714	1.446991	-2.0376
H	0.796193	1.299484	-0.43038
H	0.203372	1.334301	-2.88452
C	0.582018	-1.84028	0.56232
H	1.257914	-1.90978	1.41193

H	0.057667	-2.78633	0.441137
H	1.166052	-1.64026	-0.33166

syn-CH_3CHOO 2b VDW

C	-0.509623	-0.53389	1.228494
H	-1.52218	-0.41917	1.595534
O	0.095774	0.560711	1.135024
O	1.40183	0.51125	0.635866
O	0.661944	1.109699	-1.91522
H	0.706333	2.053867	-2.08395
H	1.062069	0.976009	-1.02287
O	-1.733619	-0.16578	-1.28318
H	-0.96557	0.337817	-1.6242
H	-2.14131	-0.57111	-2.05168
C	0.106065	-1.82222	0.897015
H	1.030117	-1.93194	1.470565
H	-0.579539	-2.64194	1.087795
H	0.405686	-1.8085	-0.15251

syn-CH_3CHOO 2b Ts

C	2.016301	-1.44053	-0.72943
H	1.057201	-1.36535	-0.2297
O	2.713686	-0.37705	-0.51602
O	4.056139	-0.44932	-1.07987
O	3.230257	0.021471	-3.32322
H	3.12047	0.960182	-3.49371
H	3.724196	-0.10568	-2.33542
O	1.285185	-1.1757	-2.43865
H	2.084807	-0.6007	-2.9235
H	1.202982	-2.00666	-2.91953
C	2.645337	-2.78831	-0.85657
H	3.120241	-3.01477	0.100737
H	1.887539	-3.54316	-1.05675
H	3.419359	-2.79442	-1.61583

syn-CH_3CHOO 2b Prd

C	-0.77238	-0.48548	0.647209
H	-1.685265	-0.15001	1.141235
O	0.11491	0.574144	0.949256
O	1.406754	0.288877	0.34957
O	0.465766	1.597606	-1.95247
H	0.257868	2.53479	-1.91159
H	1.342266	0.846776	-0.45272

O	-1.071714	-0.53223	-0.74117
H	-0.333491	1.131112	-1.66047
H	-0.458532	-1.14396	-1.16277
C	-0.311655	-1.82863	1.178469
H	-0.115646	-1.75544	2.246428
H	-1.082987	-2.57902	1.010646
H	0.608267	-2.13942	0.684703

syn-CH_3CHOO 2c VDW

C	-0.034763	-0.68861	1.288009
H	-0.895521	-0.82886	1.930715
O	0.280184	0.519829	1.165291
O	1.361972	0.803298	0.327864
O	-1.801313	-0.67467	-0.9836
H	-2.735533	-0.537	-1.15518
H	-1.344588	0.10171	-1.3693
O	-0.242327	1.490426	-1.77404
H	0.435361	1.373376	-1.06694
H	0.23842	1.497153	-2.60492
C	0.703052	-1.7841	0.653131
H	1.767101	-1.67191	0.872717
H	0.323651	-2.74761	0.97924
H	0.601561	-1.69102	-0.43024

syn-CH_3CHOO 2c Ts

C	1.363978	-0.33478	-0.39632
H	0.55971	-0.51423	0.308443
O	1.827878	0.859556	-0.2427
O	2.961576	1.148233	-1.11257
O	0.229374	-0.21072	-1.86972
H	0.283268	-1.0062	-2.41007
H	0.683607	0.613208	-2.44023
O	1.39679	1.678504	-2.90482
H	2.213411	1.546073	-2.16074
H	1.761231	1.592518	-3.78861
C	2.24454	-1.484	-0.76429
H	2.946889	-1.62926	0.059531
H	1.656786	-2.39235	-0.88185
H	2.823886	-1.26768	-1.6548

syn-CH_3CHOO 2c Prd

C	-0.448507	-0.70361	0.741169
H	-1.274501	-0.62053	1.448467

O	0.214171	0.530021	0.936784
O	1.349877	0.597902	0.032622
O	-1.042003	-0.77827	-0.54814
H	-0.397867	-1.17171	-1.14641
H	-1.011414	1.115642	-1.39543
O	-0.478382	1.868347	-1.69478
H	0.98002	1.197635	-0.6448
H	-0.596105	1.924985	-2.64603
C	0.423256	-1.90849	1.03785
H	0.838683	-1.82537	2.040258
H	-0.167992	-2.82086	0.973561
H	1.25034	-1.96389	0.330835

syn-CH_3CHOO 2d VDW

C	-0.446919	-0.50079	1.203393
H	-1.41895	-0.30573	1.639585
O	0.250279	0.536511	1.097103
O	1.511599	0.38372	0.511226
O	0.668205	1.126994	-1.96874
H	0.787923	2.068467	-2.11433
H	1.110637	0.928657	-1.10898
O	-1.789165	0.054111	-1.21141
H	-1.001025	0.495935	-1.59021
H	-2.281712	-0.28756	-1.96091
C	0.024095	-1.82901	0.800044
H	0.968609	-2.03992	1.3083
H	-0.721092	-2.58839	1.015497
H	0.256359	-1.81047	-0.26633

syn-CH_3CHOO 2d Ts

C	1.969221	-1.41795	-0.70009
H	1.019662	-1.46435	-0.1768
O	2.594709	-0.32954	-0.39357
O	3.949	-0.26769	-0.92284
O	3.295946	-0.22485	-3.26639
H	3.312497	0.648062	-3.66532
H	3.690421	-0.16095	-2.21686
O	1.198118	-1.14777	-2.39469
H	2.05507	-0.69926	-2.89961
H	0.553559	-0.44129	-2.27311
C	2.676935	-2.70044	-0.97683
H	3.241271	-2.9591	-0.07867
H	1.953348	-3.48078	-1.19467

H	3.383574	-2.60157	-1.79332

syn-CH_3CHOO 2d Prd

C	-0.787439	-0.49408	0.703389
H	-1.62445	-0.47483	1.406546
O	-0.036492	0.618513	1.136575
O	1.309955	0.57535	0.600855
O	0.7719	1.041714	-2.11323
H	0.459919	1.816538	-2.58715
H	1.199621	0.975928	-0.28534
O	-1.294408	-0.30417	-0.62484
H	-0.013754	0.513266	-1.89724
H	-1.964826	0.385521	-0.58332
C	-0.060353	-1.81766	0.745697
H	0.406058	-1.94863	1.719665
H	-0.771075	-2.62397	0.574321
H	0.711341	-1.85679	-0.01796

syn-CH_3CHOO 1a VDW

C	0.772768	-0.99668	0.444592
H	1.501951	-1.78092	0.272657
O	-0.294553	-1.19572	-0.19162
O	-1.301838	-0.25402	-0.06255
O	0.035584	1.884944	-1.18829
H	-0.609818	1.209151	-0.89686
H	-0.306268	2.250373	-2.00698
C	0.997494	0.157413	1.318185
H	1.899279	0.026297	1.90929
H	1.078972	1.060545	0.701568
H	0.116538	0.306583	1.946529

syn-CH_3CHOO 1a Ts

C	0.966416	0.277597	0.144594
H	1.849922	-0.05419	-0.39561
O	-0.073556	-0.40726	-0.17814
O	-1.254652	0.377782	0.166956
O	0.371917	1.844687	-0.88698
H	-0.568099	1.445716	-0.51562
H	0.529855	2.673577	-0.42416
C	1.167053	0.907498	1.481294
H	1.554975	0.122859	2.139246
H	1.920265	1.691142	1.430319
H	0.234625	1.280031	1.888975

syn-CH_3CHOO 1a Prd

C	0.772768	-0.99668	0.444592
H	1.501951	-1.78092	0.272657
O	-0.294553	-1.19572	-0.19162
O	-1.301838	-0.25402	-0.06255
O	0.035584	1.884944	-1.18829
H	-0.609818	1.209151	-0.89686
H	-0.306268	2.250373	-2.00698
C	0.997494	0.157413	1.318185
H	1.899279	0.026297	1.90929
H	1.078972	1.060545	0.701568
H	0.116538	0.306583	1.946529

syn-CH_3CHOO 1b VDW

C	-0.629343	1.156627	0.245742
H	-0.894329	2.171242	-0.03112
O	-1.059308	0.3129	-0.58304
O	-0.774078	-1.02136	-0.34498
O	1.975559	-0.86431	-0.55424
H	1.027892	-1.10788	-0.58424
H	2.401066	-1.34385	-1.26814
C	0.134585	0.804863	1.444974
H	1.127033	0.44881	1.143397
H	0.230377	1.659763	2.108139
H	-0.346134	-0.04243	1.939022

syn-CH_3CHOO 1b Ts

C	0.051137	0.917216	0.345251
H	0.337154	1.859959	-0.11773
O	-0.865328	0.314788	-0.3311
O	-0.844208	-1.0953	0.039966
O	1.477787	-0.37742	-0.11776
H	0.584754	-0.99771	-0.08524
H	1.689246	-0.26882	-1.05206
C	0.235007	0.790544	1.816436
H	1.248515	1.066446	2.094488
H	-0.454359	1.505069	2.278156
H	0.000125	-0.20897	2.161598

syn-CH_3CHOO 1b Prd

C	0.32387	0.646079	-0.03341
H	0.366332	1.66033	-0.44377

O	-0.8263	0.1467	-0.70657
O	-1.163676	-1.16313	-0.18538
O	1.477559	-0.08829	-0.38083
H	-0.543877	-1.72841	-0.66751
H	1.667335	0.060325	-1.31264
C	0.202011	0.664816	1.47314
H	1.05207	1.195147	1.898581
H	-0.717165	1.170188	1.762342
H	0.187523	-0.3487	1.864687

Reference

1 W. Chao, J. Hsieh, C. Chang and J. J. Lin, *Science*, 2015, **347**, 751–754.

2 M. C. Smith, C.-H. Chang, W. Chao, L.-C. Lin, K. Takahashi, K. A. Boering and J. J.-M. Lin, *J. Phys. Chem. Lett.*, 2015, **6**, 2708–2713.

3 H.-J. Werner and P. J. Knowles, *J. Chem. Phys.*, 1988, **89**, 5803.

4 S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, 1974, **8**, 61–72.

5 H.-J. Werner, *Mol. Phys.*, 1996, **89**, 645–661.

6 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.

7 B. Ruscic, *J. Phys. Chem. A*, 2013, **117**, 11940–11953.

8 Y. Scribano, N. Goldman, R. J. Saykally and C. Leforestier, *J. Phys. Chem. A*, 2006, **110**, 5411–5419.

9 C. Leforestier, *J Chem Phys*, 2014, **140**, 74106.

10 A. Shank, Y. Wang, A. Kaledin, B. J. Braams and J. M. Bowman, *J. Chem. Phys.*, 2009, **130**.

11 V. Barone, *J. Chem. Phys.*, 2005, **122**, 1–10.

12 A. K. Samanta, L. C. Ch and H. Reisler, *Chem. Phys. Lett.*, 2013, **575**, 1–11.

13 A. B. Ryzhkov and P. A. Ariya, *Chem Phys Lett*, 2003, **367**, 423–429.

14 A. B. Ryzhkov and P. A. Ariya, *Phys. Chem. Chem. Phys.*, 2004, **6**, 5042–5050.

15 A. B. Ryzhkov and P. A. Ariya, *Chem Phys Lett*, 2006, **419**, 479–485.