The Tropospheric Oxidation of Methyl hydrotrioxide (CH_3OOOH) by Hydroxyl Radical

*Josep M. Anglada, *[a] and Albert Solé [b]*

a) Departament de Química Biològica, (IQAC – CSIC), Jordi Girona, 18-26, E-08034 Barcelona. E-mail: anglada@iqac.csic.es.

b) Departament de Ciència de Materials i Química Física, i Institut de Química Teòrica i Computacional (IQTCUB). Universitat de Barcelona, Martí i Franqués, 1, E-08028 Barcelona. E-mail: a.sole@ub.edu

(Supplementary information)

Regarding the technical details with respect to single point CCSD(T) energy calculations, in Figure S1 we have plotted the electronic densities of the HOMO and SOMO natural orbitals of the **ATS1a** stationary point. The BH&HLYP approach describes correctly the electronic features of the hydrogen atom abstraction by the hydroxyl radical. The process involves the breaking and making of the (CH_3OO)O-H bond and H-O(H) covalent bonds and is described by a three electron-three center system where the electron density lies over the O-H-O bonds. The figure also shows that the HF approach does not describe this situation correctly. The SCF procedure falls to a solution where the unpaired electron has a wrong orientation, and any attempt to rotate the orbitals in order to get the correct wavefunction was unsuccessful at this level of theory. Consequently, the CCSD expansion over this HF wavefunction has no meaning in correctly describe the process investigated. With a CASSCF(1,2) approach we could obtain the right wave function and we have performed the coupled cluster expansion over a CASSCF(1,2) wavefunction for all single point CCSD(T) calculations of all transition states. The same procedure has been applied in the *s* points close to the transition state in the calculations for the IVTST kinetic study.

Regarding the CASSCF and CASPT2 calculations, the active space in the CASSCF calculations has been chosen according to the fractional occupation of the natural orbitals [1] generated from an MRDCI[2] or QCISD[3] wave function, which are based on the correlation of all valence electrons. In these cases, the final energy was obtained by carrying our single point CASPT2[4] calculations over a CASSCF wave function using the aug-cc-pVTZ basis set. The composition of the CASSCF active space for the search of

the stationary points include 11 electrons in 10 orbitals, that corresponds to the σ(OH), σ(CO), σ(OO), and σ(O-OH), their corresponding anti-bonding orbitals, the π(COO) orbital, and a combination of π*(COO) with π(OH) orbitals , in the same way as described for the reaction of H_2COO with OH.[5] The CASSCF for the CASPT2 single point energy calculations include 17 electrons and 14 orbitals that correspond to the sum of the active spaces of carbonyl oxide and hydroxyl radical (CASSCF(12,9) for H_2COO and CASSCF(5,5) for OH), as has been done in the study of the H_2COO + OH reaction.[5]

Regarding the calculation at the IVTST level, we have employed a dual approach, namely computing, at different *s* points along the potential energy surface, the hessian matrices with the BH&HLYP approach and energies obtained at CCSD(T) level of theory. The calculations have been done at *s* = 0.104, 0.209, 0.627, 1.045, 1.464, 1,882, 2.300, 2.719, 3.137, 3.974, and 4.601 in the path to the reaction products, and *s* = 0.042, 0.084, 0.105, 0.125, 1.045, 1.464, 1.882, 2.301, 2.719, 3.137, 3.973, and 4.600 in the path to the reactants (these s points corresponds to the reactions through **ATS1b)**. For the remaining reaction paths, the same number of *s* points have been considered and the corresponding *s* values are close to these). The CCSD(T) calculations in the *s* points close to the transition state (two in the path to the products and four in the path to reactants) have been done over a CASSCF(1,2) wave function for the reasons discussed in the previous paragraph. Along the path to the reactants, there are some points where the T1 diagnostic of CCSD expansion showed multi referential character (for instance T1d=0.063 at s=0.209), implying that the CCSD(T) energy values at these points is not reliable and consequently have been omitted in the kinetic study.

The rate constants obtained with the CTST calculations are collected in Table S6, S7, and S9. Our results show that the CTST approach predict the rate constants to be about one order of magnitude greater than IVTST for both, reactions 7 and 8. In addition, the tunneling parameters are predicted to be much greater with the ZCT approach and with the Wigner expression relative to the SCT computed at IVTST level, that is, between 3 and 4 times for **ATS1a** and **ATS1b** at ZCT level, and about 7 times bot **ATS2a** and **ATS2c** at ZCT and Wigner level, and up to 300 times greater for **ATS2b** with ZCT level. This is due to the sharper potential energy surface (PES) predicted by the BH&HLYP approach, which is modulated in performing the CCSD(T) single point energy calculations at different *s* points along the PES. With these tunneling corrections, figures

S7 and S8 shown that the CTST calculations predict both reaction 7 and reaction 8 to have negative temperature dependence.

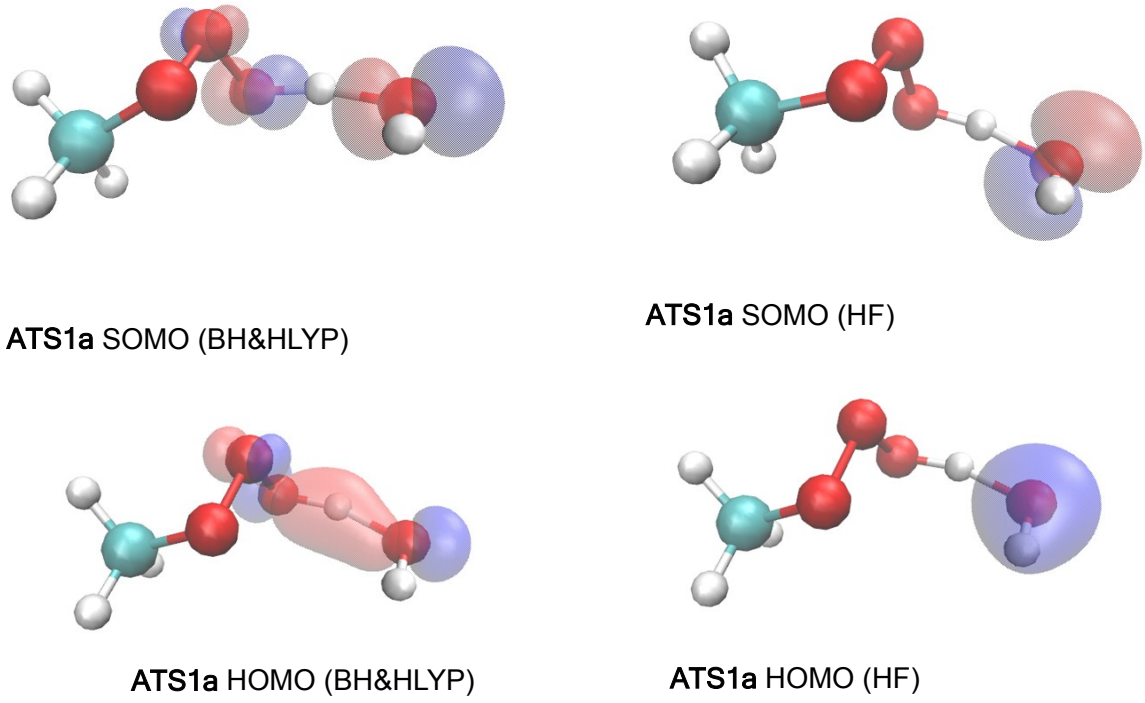

Figure S1: Electronic features of the HOMO and SOMO natural orbitals for the **ATS1a** stationary point computed at BH&HLYP and HF theoretical approaches.

Table S1: Relative energies and energies plus ZPE (in kcal·mol^{-1}), enthalpies and free energies (in kcal·mol^{-1}, at 298 K) calculated for isomerization of CH_3OOOH .[a]

Compound	ΔE	Δ (E+ZPE)	ΔH (298K)	ΔG(298K)
***trans*-CH_3OOOH ⇌ *cis*-CH_3OOOH**				
***trans*-CH_3OOOH**	0.00	0.00	0.00	0.00
RTS2	5.11	4.54	4.36	4.63
RTS3	6.66	5.98	5,85	5.95
RTS4	9.69	9.49	9.04	9.93
RTS1	4.39	4.13	3.77	4.54
***cis*-CH_3OOOH**	2.45	2.32	2.36	2.24

a) Energies computed at CCSD(T)/CBS//BH&HLYP/6-311+G(2df,2p) with ZPE and thermodynamic corrections computed at BH&HLYP/6-311+G(2df,2p) level.

Table S2. Equilibrium constants for the isomerization between the *trans*-CH_3OOOH and *cis*-CH_3OOOH conformers (K_{eq}) and rate constants for the *trans* – *cis* interconversion through the four different transition states (k_{RTX}, in s^{-1}). These values have been computed in the range of temperatures between 225 – 325 K.

T	K_{eq}	k_{RTS1}	k_{RTS2}	k_{RTS3}	k_{RTS4}
225.0	.6400E-02	2.82E+08	1.67E+08	8.16E+06	1.70E+03
230.0	.7180E-02	3.48E+08	2.12E+08	1.11E+07	2.72E+03
240.0	.8908E-02	5.17E+08	3.32E+08	1.99E+07	6.54E+03
250.0	.1087E-01	7.45E+08	5.01E+08	3.41E+07	1.46E+04
260.0	.1305E-01	1.04E+09	7.33E+08	5.61E+07	3.09E+04
270.0	.1547E-01	1.42E+09	1.04E+09	8.88E+07	6.15E+04
275.0	.1677E-01	1.65E+09	1.23E+09	1.10E+08	8.53E+04
280.0	.1812E-01	1.90E+09	1.45E+09	1.36E+08	1.17E+05
290.0	.2099E-01	2.49E+09	1.97E+09	2.03E+08	2.12E+05
298.0	.2344E-01	3.05E+09	2.48E+09	2.74E+08	3.32E+05
300.0	.2408E-01	3.20E+09	2.62E+09	2.95E+08	3.70E+05
310.0	.2738E-01	4.05E+09	3.43E+09	4.18E+08	6.23E+05
325.0	.3273E-01	5.62E+09	4.97E+09	6.78E+08	1.28E+06

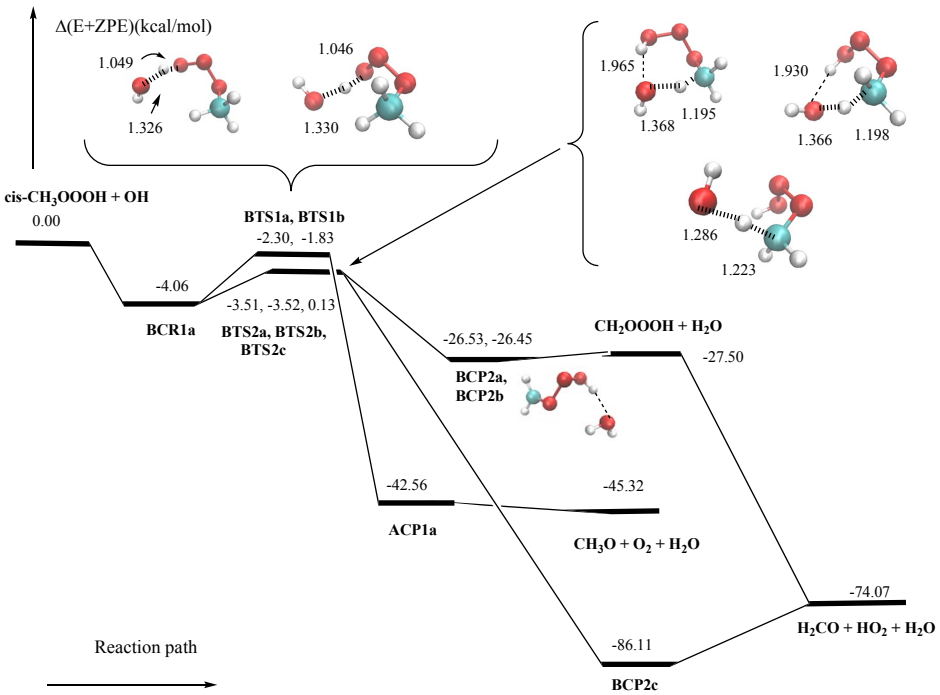

Figure S2: Schematic potential energy surface for the reaction between *cis*-CH_3OOOH and OH.

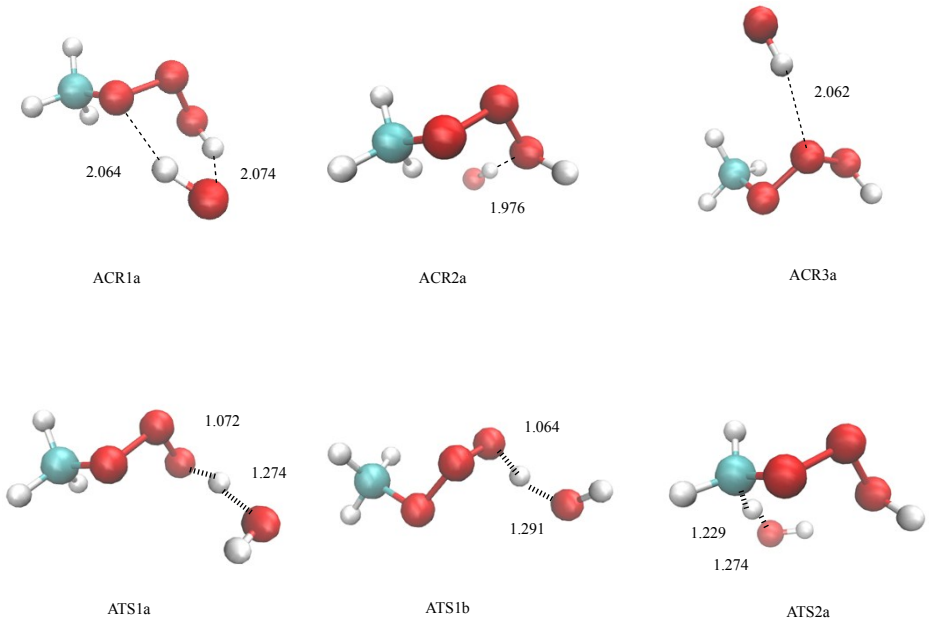

Figure S3: Schematic stationary points for the reaction between CH_3OOOH + OH

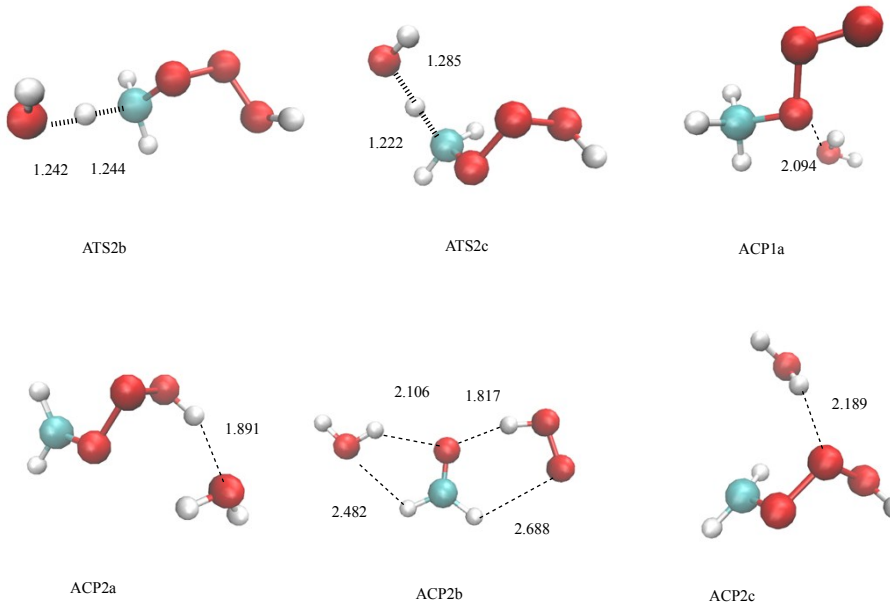

Figure S4: Schematic stationary points for the reaction between CH_3OOOH + OH (continuation)

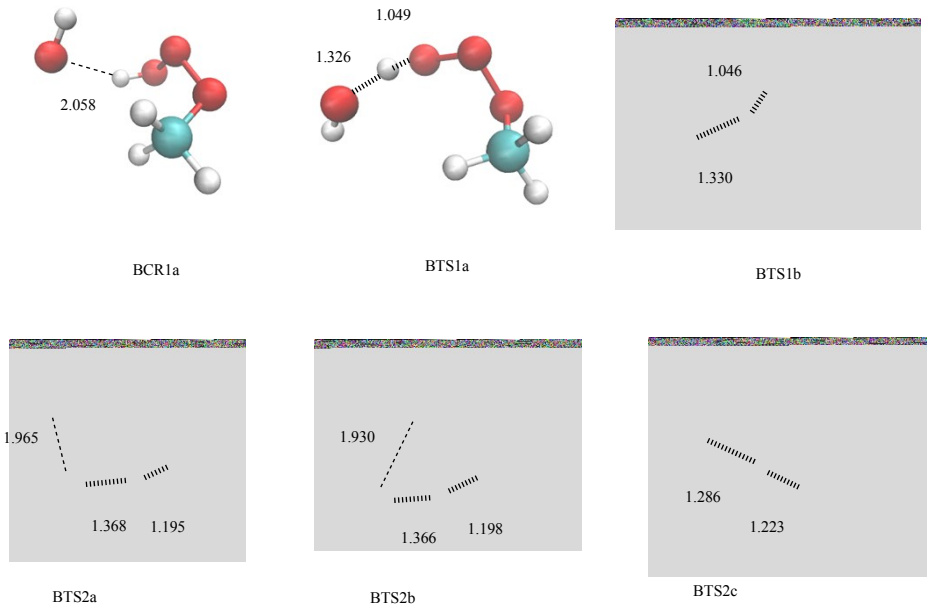

Figure S5: Schematic stationary points for the reaction between CH_3OOOH + OH (continuation)

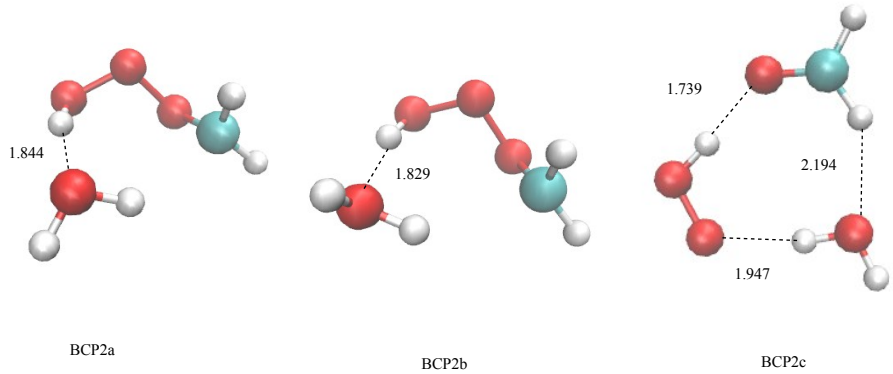

Figure S6: Schematic stationary points for the reaction between CH_3OOOH + OH (continuation)

Table S3. Relative energies and energies plus ZPE (in kcal·mol^{-1}), enthalpies and free energies (in kcal·mol^{-1}, at 298K), calculated for the unimolecular decomposition of CH_2OOOH.[a]

Compound	Method	ΔE	Δ(E+ZPE)	ΔH(298K)	ΔG(298K)
CH_2OOOH	**A/B**	0.00	0.00	0.00	0.00
CTS1	**A**	0.23	-0.93	-1.02	-0.92
	B	-0.50	-1.85	-1.89	-1.92
$H_2CO\cdots HO_2$ (CCP1)	**A**	-59.33	-59.48	-58.78	-60.99
$H_2CO + HO_2$	**A**	-50.12	-52.34	-51.37	-61.83
CTS2	**A**	12.18	10.12	10.17	10.13
	B	9.09	6.86	7.03	6.57

$H_2COO\cdots OH$ (CCP2)	**A**	0.58	-0.43	-0.22	-1.11
H_2COO + OH	**A**	9.20	6.03	6.94	-2.11

a) **A** stands for energies computed at CCSD(T)/CBS//BH&HLYP/6-311+G(2df,2p) level of theory, and the ZPE and, the enthalpic, and entropic corrections have been computed at BH&HLYP/6-311+G(2df,2p) level of theory. **B** stands for energies computed at CASPT2(17,14)/aug-cc-pVTZ//CASSCF(11,10)/6-311+G(2df,2p) with ZPE, enthalpic, and entropic corrections calculated at CASSCF(11,10)/6-311+G(2df,2p)

Table S4. Relative energies and energies plus ZPE (in kcal·mol^{-1}), enthalpies and free energies (in kcal·mol^{-1}, at 298K), calculated for the unimolecular decomposition of CH_3OOO.[a]

Compound	Method	ΔE	Δ(E+ZPE)	ΔH(298K)	ΔG(298K)
***cis*-CH_3OOO**	A/B	0.00	0.00	0.00	0.00
***trans*-CH_3OOO**	A	2.14	2.12	2.24	1.83
DTS1	A	7.29	5.73	5.81	5.46
DTS2	A	8.90	7.19	7.40	6.62
DTS3	B	5.0	4.89	4.43	5.40
$CH_3O + O_2$ ($X^3\Sigma^-$)	A	2.50	-0.80	0.18	-10.26
	B	255	-0.76	0.22	-10.22

b) **A** stands for energies computed at CCSD(T)/CBS//CCSD(T)/aug-cc-pVTZ level of theory, and the ZPE and, the enthalpic, and entropic corrections have been computed at QCISD/6-311+G(2df,2p) level of theory. **B** stands for energies computed at CCSD(T)/CBS//CCSD(T)/ 6-311+G(2df,2p) level of theory, and the ZPE and, the enthalpic, and entropic corrections have been computed at QCISD/6-311+G(2df,2p) level of theory

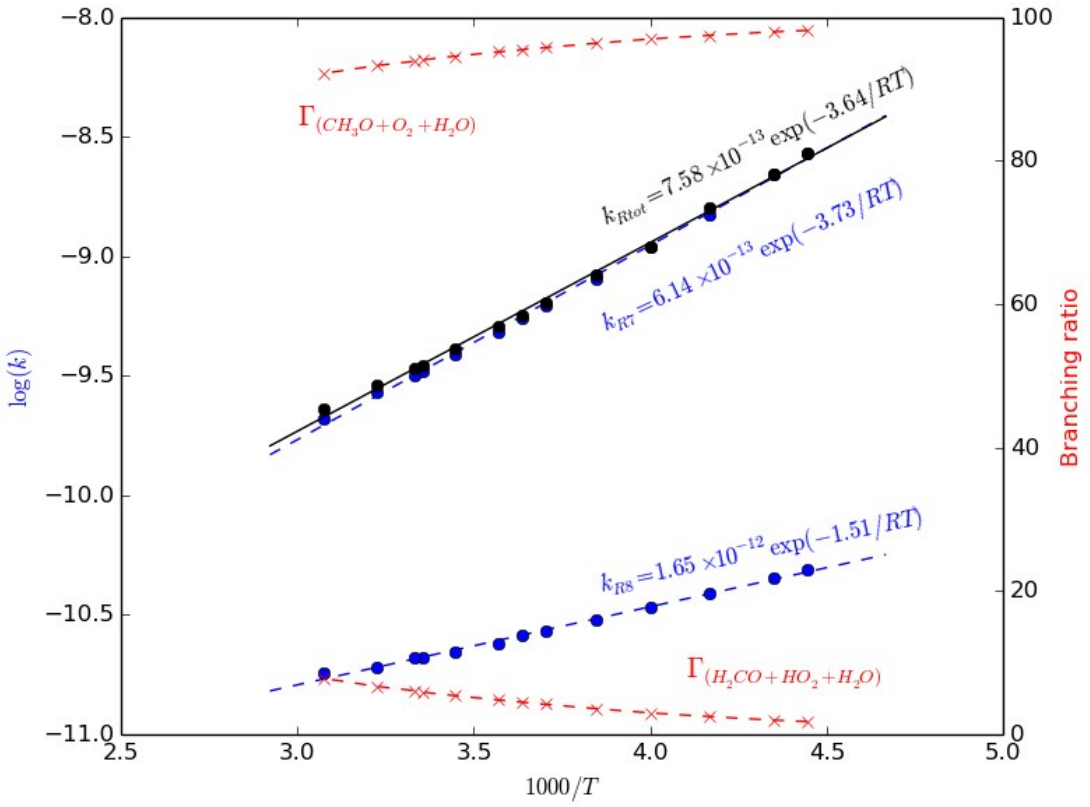

Figure S7: Computed Arrhenius plot for reaction 7 and 8 (in blue) and the overall R_{tot} = reaction 7 + reaction 8 in black, and the branching ratios (in red), computed with the CTST level considering the tunneling effect with the ZCT approach. The corresponding Arrhenius equations are also given.

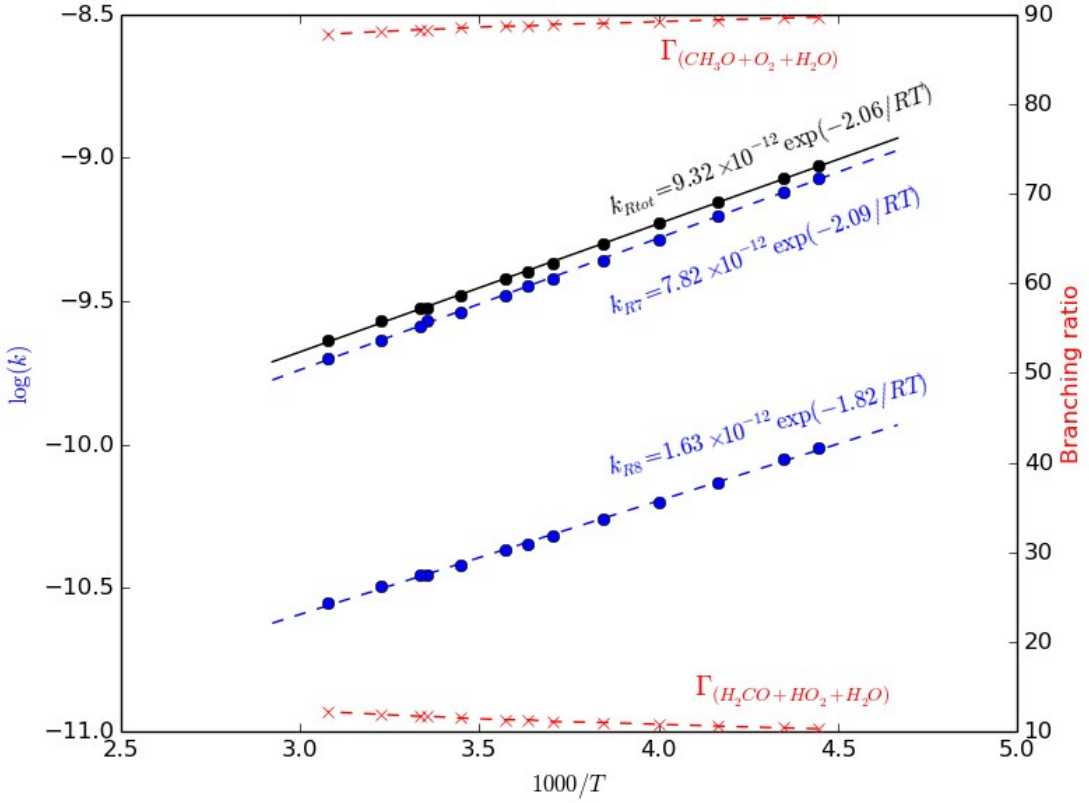

Figure S8: Computed Arrhenius plot for reaction 7 and 8 (in blue) and the overall R_{tot} = reaction 7 + reaction 8 in black, and the branching ratios (in red), computed with the CTST level considering the tunneling effect with the Wigner expression. The corresponding Arrhenius equations are also given.

Table S5. Total calculated rate constants at IVTST level (in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) and the corresponding branching rations (in %) in the 215-325 K range of temperatures.

T	$k_{TOTAL\text{-}IVTST}$	$\Gamma_{R7\text{-}IVTST}$	$\Gamma_{R8\text{-}IVTST}$
225.0	1.5e-10	99.0	1.0
230.0	1.4e-10	98.9	1.1
240.0	1.1e-10	98.6	1.4
250.0	9.2e-11	98.2	1.8
260.0	7.8e-11	97.7	2.3
270.0	6.8e-11	97.3	2.7
275.0	6.4e-11	97.0	3.0
280.0	6.0e-11	96.7	3.3
290.0	5.3e-11	96.2	3.8
298.0	4.9e-11	95.7	4.3
300.0	4.9e-11	95.6	4.4
310.0	4.4e-11	94.9	5.1
325.0	4.0e-11	93.9	6.1

Table S6. Total calculated rate constants at CTST level (in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) considering the tunneling with the ZCT approach and according to the Wigner expression. The corresponding branching rations (in %) in the 215-325 K range of temperatures.

T	$k_{TOTAL-(ZCT)}$	$k_{TOTAL-(wig)}$	$\Gamma_{R7-(ZCT)}$	$\Gamma_{R8-(ZCT)}$	$\Gamma_{R7-(wig)}$	$\Gamma_{R8-(wig)}$
225.0	2.7e-09	9.4e-10	98.2	1.8	89.7	10.3
230.0	2.2e-09	8.5e-10	98.0	2.0	89.6	10.4
240.0	1.6e-09	7.0e-10	97.5	2.5	89.4	10.6
250.0	1.1e-09	5.9e-10	97.0	3.0	89.2	10.8
260.0	8.4e-10	5.0e-10	96.4	3.6	89.0	11.0
270.0	6.4e-10	4.3e-10	95.8	4.2	88.9	11.1
275.0	5.7e-10	4.0e-10	95.5	4.5	88.7	11.3
280.0	5.1e-10	3.8e-10	95.2	4.8	88.7	11.3
290.0	4.1e-10	3.3e-10	94.6	5.4	88.5	11.5
298.0	3.5e-10	3.0e-10	94.1	5.9	88.3	11.7
300.0	3.4e-10	3.0e-10	93.9	6.1	88.3	11.7
310.0	2.9e-10	2.7e-10	93.3	6.7	88.1	11.9
325.0	2.3e-10	2.3e-10	92.2	7.8	87.8	12.2

Table S7. Calculated rate constants for R7 and R8 at IVTST and CTST with tunneling corrections at ZCT and Wigner levels (in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) in the 215-325 K range of temperatures. [a,b]

	$k_{R7-total}$			$k_{R8-total}$		
T	$k_{(IVTST)}$	$k_{(CTST-ZCT)}$	$k_{(CTST-wig)}$	$k_{(IVTST)}$	$k_{(CTST-ZCT)}$	$k_{(CTST-wig)}$
225.0	1.5e-10	2.7e-09	8.5e-10	1.5e-12	4.9e-11	9.7e-11
230.0	1.4e-10	2.2e-09	7.6e-10	1.5e-12	4.5e-11	8.9e-11
240.0	1.1e-10	1.5e-09	6.3e-10	1.6e-12	3.9e-11	7.4e-11
250.0	9.1e-11	1.1e-09	5.2e-10	1.7e-12	3.4e-11	6.3e-11
260.0	7.7e-11	8.1e-10	4.4e-10	1.8e-12	3.0e-11	5.5e-11
270.0	6.6e-11	6.2e-10	3.8e-10	1.9e-12	2.7e-11	4.8e-11
275.0	6.2e-11	5.5e-10	3.6e-10	1.9e-12	2.6e-11	4.5e-11
280.0	5.8e-11	4.8e-10	3.3e-10	2.0e-12	2.4e-11	4.3e-11
290.0	5.1e-11	3.9e-10	2.9e-10	2.1e-12	2.2e-11	3.8e-11
298.0	4.7e-11	3.3e-10	2.7e-10	2.1e-12	2.1e-11	3.5e-11
300.0	4.7e-11	3.2e-10	2.6e-10	2.2e-12	2.1e-11	3.5e-11
310.0	4.2e-11	2.7e-10	2.3e-10	2.3e-12	1.9e-11	3.2e-11
325.0	3.8e-11	2.1e-10	2.0e-10	2.4e-12	1.8e-11	2.8e-11

a) $K_{R7-total}$ corresponds to formation of $CH_3O + O_2 + H_2O$.
b) $K_{R8-total}$ corresponds to formation of $H_2CO + HO_2 + H_2O$

Table S8*:* Equilibrium constants for the formation of the pre-reactive complexes (K_{eq} in $cm^3 \cdot molecule^{-1}$); tunneling parameter (κ); unimolecular rate constant for each elementary process (k_2 in s^{-1}), computed at IVTST level, and total rate constant for each elementary

reaction ($k_{total} = \kappa K_{eq} \cdot k_2$, in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$), computed at different temperatures (T in kelvin) for all elementary reactions investigated.

T	K_{eq}	κ	k_2	k
ATS1a				
225.0	6.7e-20	14.77	1.9e+08	1.5e-10
230.0	5.1e-20	13.30	2.4e+08	1.3e-10
240.0	3.1e-20	10.97	3.8e+08	1.1e-10
250.0	2.0e-20	9.28	5.6e+08	8.6e-11
260.0	1.3e-20	8.00	8.1e+08	7.2e-11
270.0	8.7e-21	7.01	1.1e+09	6.2e-11
275.0	7.3e-21	6.58	1.3e+09	5.7e-11
280.0	6.1e-21	6.22	1.6e+09	5.4e-11
290.0	4.4e-21	5.57	2.1e+09	4.7e-11
298.0	3.4e-21	5.17	2.6e+09	4.3e-11
300.0	3.2e-21	5.08	2.8e+09	4.2e-11
310.0	2.4e-21	4.63	3.6e+09	3.8e-11
325.0	1.6e-21	4.12	5.1e+09	3.3e-11
ATS1b				
225.0	6.7e-20	3.33	7.0e+07	4.6e-12
230.0	5.1e-20	3.11	8.8e+07	4.5e-12
240.0	3.1e-20	2.79	1.4e+08	4.3e-12
250.0	2.0e-20	2.53	2.1e+08	4.1e-12
260.0	1.3e-20	2.33	3.2e+08	4.1e-12
270.0	8.7e-21	2.17	4.6e+08	4.0e-12
275.0	7.3e-21	2.11	5.5e+08	4.0e-12
280.0	6.1e-21	2.05	6.6e+08	4.0e-12
290.0	4.4e-21	1.95	9.1e+08	4.0e-12
298.0	3.4e-21	1.87	1.2e+09	4.0e-12
300.0	3.2e-21	1.86	1.2e+09	4.0e-12
310.0	2.4e-21	1.78	1.7e+09	4.0e-12
325.0	1.6e-21	1.68	2.5e+09	4.1e-12
BTS1a				
225.0	2.3e-20	2.58	1.4e+09	6.9e-11
230.0	1.9e-20	2.46	1.6e+09	6.4e-11
240.0	1.4e-20	2.27	2.1e+09	5.6e-11
250.0	1.0e-20	2.11	2.7e+09	5.0e-11
260.0	7.5e-21	1.99	3.4e+09	4.5e-11
270.0	5.8e-21	1.89	4.2e+09	4.1e-11
275.0	5.1e-21	1.84	4.6e+09	3.9e-11
280.0	4.6e-21	1.80	5.0e+09	3.8e-11
290.0	3.7e-21	1.73	6.0e+09	3.5e-11
298.0	3.1e-21	1.67	6.8e+09	3.3e-11
300.0	3.0e-21	1.66	7.0e+09	3.3e-11
310.0	2.5e-21	1.60	8.2e+09	3.1e-11
325.0	1.9e-21	1.54	1.0e+10	2.9e-11
BTS1b				
225.0	2.3e-20	7.08	4.1e+08	6.7e-11
230.0	1.9e-20	6.41	5.0e+08	6.2e-11
240.0	1.4e-20	5.41	7.3e+08	5.4e-11

250.0	1.0e-20	4.65	1.0e+09	4.8e-11
260.0	7.5e-21	4.12	1.4e+09	4.4e-11
270.0	5.8e-21	3.68	1.9e+09	4.1e-11
275.0	5.1e-21	3.50	2.2e+09	4.0e-11
280.0	4.6e-21	3.34	2.6e+09	3.9e-11
290.0	3.7e-21	3.07	3.3e+09	3.7e-11
298.0	3.1e-21	2.88	4.0e+09	3.6e-11
300.0	3.0e-21	2.84	4.2e+09	3.5e-11
310.0	2.5e-21	2.65	5.2e+09	3.4e-11
325.0	1.9e-21	2.42	7.2e+09	3.3e-11
ATS2a				
225.0	1.2e-21	1.51	4.2e+08	7.3e-13
230.0	1.0e-21	1.48	4.9e+08	7.3e-13
240.0	7.8e-22	1.43	6.7e+08	7.5e-13
250.0	6.2e-22	1.38	8.8e+08	7.6e-13
260.0	5.1e-22	1.35	1.1e+09	7.8e-13
270.0	4.2e-22	1.33	1.4e+09	8.0e-13
275.0	3.8e-22	1.31	1.6e+09	8.1e-13
280.0	3.5e-22	1.30	1.8e+09	8.2e-13
290.0	3.0e-22	1.27	2.2e+09	8.4e-13
298.0	2.7e-22	1.26	2.6e+09	8.6e-13
300.0	2.6e-22	1.26	2.6e+09	8.7e-13
310.0	2.3e-22	1.23	3.2e+09	8.9e-13
325.0	1.9e-22	1.21	4.0e+09	9.2e-13
ATS2b				
225.0	6.7e-20	1.53	1.3e+05	1.4e-14
230.0	5.1e-20	1.50	2.0e+05	1.6e-14
240.0	3.1e-20	1.45	4.6e+05	2.0e-14
250.0	2.0e-20	1.40	9.5e+05	2.6e-14
260.0	1.3e-20	1.37	1.9e+06	3.3e-14
270.0	8.7e-21	1.34	3.5e+06	4.1e-14
275.0	7.3e-21	1.32	4.7e+06	4.5e-14
280.0	6.1e-21	1.31	6.3e+06	5.0e-14
290.0	4.4e-21	1.28	1.1e+07	6.1e-14
298.0	3.4e-21	1.26	1.6e+07	7.1e-14
300.0	3.2e-21	1.26	1.8e+07	7.4e-14
310.0	2.4e-21	1.24	2.9e+07	8.8e-14
325.0	1.6e-21	1.22	5.6e+07	1.1e-13
ATS2c [a]				
225.0	2.9e-22	1.45 (1.48)	1.1e+09	4.9e-13 (4.6e-13)
230.0	2.6e-22	1.42 (1.45)	1.3e+09	5.0e-13 (4.8e-13)
240.0	2.2e-22	1.38 (1.41)	1.8e+09	5.4e-13 (5.1e-13)
250.0	1.8e-22	1.34 (1.37)	2.4e+09	5.7e-13 (5.6e-13)
260.0	1.5e-22	1.31 (1.33)	3.0e+09	6.1e-13 (6.0e-13)
270.0	1.3e-22	1.28 (1.30)	3.8e+09	6.4e-13 (6.3e-13)
275.0	1.2e-22	1.27 (1.29)	4.2e+09	6.6e-13 (6.5e-13)
280.0	1.2e-22	1.26 (1.28)	4.7e+09	6.8e-13 (6.7e-13)
290.0	1.0e-22	1.24 (1.26)	5.7e+09	7.2e-13 (7.1e-13)

298.0	9.3e-23	1.22 (1.24)	6.6e+09	7.5e-13 (7.4e-13)
300.0	9.1e-23	1.22 (1.24)	6.8e+09	7.6e-13 (7.5e-13)
310.0	8.2e-23	1.21 (1.22)	8.1e+09	8.0e-13 (7.9e-13)
325.0	7.1e-23	1.19 (1.20)	1.0e+10	8.6e-13 (8.6e-13)
BTS2a				
225.0	2.3e-20	1.23	9.0e+08	2.6e-11
230.0	1.9e-20	1.23	1.0e+09	2.4e-11
240.0	1.4e-20	1.21	1.3e+09	2.1e-11
250.0	1.0e-20	1.18	1.6e+09	1.8e-11
260.0	7.5e-21	1.17	1.9e+09	1.6e-11
270.0	5.8e-21	1.16	2.2e+09	1.5e-11
275.0	5.1e-21	1.15	2.4e+09	1.4e-11
280.0	4.6e-21	1.14	2.6e+09	1.3e-11
290.0	3.7e-21	1.13	3.0e+09	1.2e-11
298.0	3.1e-21	1.13	3.3e+09	1.2e-11
300.0	3.0e-21	1.12	3.4e+09	1.1e-11
310.0	2.5e-21	1.12	3.8e+09	1.1e-11
325.0	1.9e-21	1.10	4.6e+09	9.6e-12
BTS2b				
225.0	2.3e-20	2.34	2.8e+08	1.5e-11
230.0	1.9e-20	2.25	3.3e+08	1.4e-11
240.0	1.4e-20	2.10	4.5e+08	1.3e-11
250.0	1.0e-20	1.98	6.0e+08	1.2e-11
260.0	7.5e-21	1.89	7.7e+08	1.1e-11
270.0	5.8e-21	1.80	9.7e+08	1.0e-11
275.0	5.1e-21	1.76	1.1e+09	9.8e-12
280.0	4.6e-21	1.73	1.2e+09	9.5e-12
290.0	3.7e-21	1.66	1.5e+09	9.0e-12
298.0	3.1e-21	1.62	1.7e+09	8.6e-12
300.0	3.0e-21	1.61	1.8e+09	8.6e-12
310.0	2.5e-21	1.56	2.1e+09	8.2e-12
325.0	1.9e-21	1.50	2.7e+09	7.7e-12
BTS2c				
225.0	2.3e-20	1.38	2.5e+07	8.1e-13
230.0	1.9e-20	1.36	3.2e+07	8.3e-13
240.0	1.4e-20	1.32	4.9e+07	8.8e-13
250.0	1.0e-20	1.29	7.2e+07	9.3e-13
260.0	7.5e-21	1.25	1.0e+08	9.8e-13
270.0	5.8e-21	1.24	1.4e+08	1.0e-12
275.0	5.1e-21	1.22	1.7e+08	1.1e-12
280.0	4.6e-21	1.22	2.0e+08	1.1e-12
290.0	3.7e-21	1.20	2.6e+08	1.1e-12
298.0	3.1e-21	1.19	3.2e+08	1.2e-12
300.0	3.0e-21	1.19	3.4e+08	1.2e-12
310.0	2.5e-21	1.17	4.3e+08	1.3e-12
325.0	1.9e-21	1.15	6.1e+08	1.3e-12

a) In order to check the reliability of equations 1-2, we have also calculated for **ATS2c** the rate constants considering the bimolecular reaction directly. The corresponding calculated values are written in parenthesis.

Table S9*:* Equilibrium constants for the formation of the pre-reactive complexes (K_{eq} in $cm^3 \cdot molecule^{-1}$); tunneling parameter with the ZCT approach (κ_{ZCT}) and using the Wigner formula (κ_{wig}); unimolecular rate constant for each elementary process (k_2 in s^{-1}), and total rate constant for each elementary reaction ($k_{total} = \kappa\ K_{eq} \cdot k_2$, in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, $k_{total\text{-}ZCT}$ considering the ZCT tunneling and $k_{total\text{-}wig}$ with the Wigner formula); computed at different temperatures (T in kelvin) for all elementary reactions investigated.

T	Keq	κ_{ZCT}	κ_{wig}	k_2	$k_{total\text{-}ZCT}$	$k_{total\text{-}wig}$
ATS1a						
225.0	6.7e-20	30.25	10.05	9.8e+08	2.0e-09	6.6e-10
230.0	5.1e-20	26.64	9.66	1.2e+09	1.6e-09	5.9e-10
240.0	3.1e-20	20.88	8.95	1.7e+09	1.1e-09	4.7e-10
250.0	2.0e-20	16.85	8.32	2.4e+09	7.8e-10	3.9e-10
260.0	1.3e-20	13.87	7.77	3.2e+09	5.8e-10	3.2e-10
270.0	8.7e-21	11.63	7.30	4.3e+09	4.4e-10	2.7e-10
275.0	7.3e-21	10.71	7.05	4.9e+09	3.8e-10	2.5e-10
280.0	6.1e-21	9.91	6.85	5.6e+09	3.4e-10	2.3e-10
290.0	4.4e-21	8.58	6.45	7.1e+09	2.7e-10	2.0e-10
298.0	3.4e-21	7.70	6.15	8.6e+09	2.3e-10	1.8e-10
300.0	3.2e-21	7.51	6.09	9.0e+09	2.2e-10	1.8e-10
310.0	2.4e-21	6.68	5.77	1.1e+10	1.8e-10	1.6e-10
325.0	1.6e-21	5.68	5.35	1.5e+10	1.4e-10	1.3e-10
ATS1b						
225.0	6.7e-20	41.57	8.98	2.6e+08	7.1e-10	1.5e-10
230.0	5.1e-20	35.51	8.63	3.2e+08	5.8e-10	1.4e-10
240.0	3.1e-20	26.88	8.00	4.9e+08	4.1e-10	1.2e-10
250.0	2.0e-20	21.07	7.47	7.3e+08	3.0e-10	1.1e-10
260.0	1.3e-20	16.92	6.99	1.0e+09	2.3e-10	9.3e-11
270.0	8.7e-21	13.84	6.53	1.5e+09	1.8e-10	8.3e-11
275.0	7.3e-21	12.63	6.32	1.7e+09	1.6e-10	7.9e-11
280.0	6.1e-21	11.61	6.18	2.0e+09	1.4e-10	7.5e-11
290.0	4.4e-21	9.85	5.79	2.7e+09	1.1e-10	6.7e-11
298.0	3.4e-21	8.76	5.56	3.3e+09	9.9e-11	6.3e-11
300.0	3.2e-21	8.51	5.50	3.5e+09	9.6e-11	6.2e-11
310.0	2.4e-21	7.44	5.20	4.5e+09	8.1e-11	5.7e-11
325.0	1.6e-21	6.23	4.82	6.4e+09	6.5e-11	5.0e-11
BTS1a						
225.0	2.3e-20	4.22	7.65	1.3e+10	1.3e-09	2.3e-09
230.0	1.9e-20	3.98	7.36	1.4e+10	1.1e-09	2.0e-09
240.0	1.4e-20	3.60	6.85	1.7e+10	8.3e-10	1.6e-09
250.0	1.0e-20	3.30	6.37	1.9e+10	6.4e-10	1.2e-09
260.0	7.5e-21	3.03	5.95	2.2e+10	5.0e-10	9.9e-10
270.0	5.8e-21	2.82	5.60	2.5e+10	4.1e-10	8.1e-10

275.0	5.1e-21	2.73	5.46	2.6e+10	3.7e-10	7.3e-10
280.0	4.6e-21	2.64	5.27	2.8e+10	3.3e-10	6.7e-10
290.0	3.7e-21	2.49	4.98	3.1e+10	2.8e-10	5.6e-10
298.0	3.1e-21	2.38	4.80	3.3e+10	2.4e-10	4.9e-10
300.0	3.0e-21	2.36	4.75	3.4e+10	2.4e-10	4.8e-10
310.0	2.5e-21	2.24	4.50	3.7e+10	2.0e-10	4.1e-10
325.0	1.9e-21	2.10	4.20	4.2e+10	1.7e-10	3.3e-10
BTS1b						
225.0	2.3e-20	3.19	6.64	2.5e+10	1.9e-09	3.9e-09
230.0	1.9e-20	3.05	6.43	2.7e+10	1.6e-09	3.4e-09
240.0	1.4e-20	2.81	5.96	3.1e+10	1.2e-09	2.5e-09
250.0	1.0e-20	2.61	5.58	3.5e+10	9.2e-10	2.0e-09
260.0	7.5e-21	2.44	5.25	4.0e+10	7.3e-10	1.6e-09
270.0	5.8e-21	2.30	4.93	4.4e+10	5.9e-10	1.3e-09
275.0	5.1e-21	2.25	4.79	4.6e+10	5.3e-10	1.1e-09
280.0	4.6e-21	2.18	4.65	4.9e+10	4.8e-10	1.0e-09
290.0	3.7e-21	2.07	4.40	5.3e+10	4.0e-10	8.6e-10
298.0	3.1e-21	2.00	4.24	5.7e+10	3.5e-10	7.5e-10
300.0	3.0e-21	1.99	4.18	5.8e+10	3.4e-10	7.2e-10
310.0	2.5e-21	1.90	3.98	6.3e+10	2.9e-10	6.1e-10
325.0	1.9e-21	1.81	3.71	7.0e+10	2.4e-10	4.9e-10
ATS2a						
225.0	1.2e-21	6.59	6.77	1.7e+09	1.3e-11	1.3e-11
230.0	1.0e-21	6.13	6.51	1.9e+09	1.1e-11	1.2e-11
240.0	7.8e-22	5.35	6.05	2.3e+09	9.6e-12	1.1e-11
250.0	6.2e-22	4.74	5.66	2.7e+09	8.1e-12	9.7e-12
260.0	5.1e-22	4.28	5.29	3.2e+09	7.1e-12	8.7e-12
270.0	4.2e-22	3.86	4.99	3.8e+09	6.2e-12	8.0e-12
275.0	3.8e-22	3.70	4.84	4.1e+09	5.8e-12	7.6e-12
280.0	3.5e-22	3.54	4.72	4.4e+09	5.5e-12	7.3e-12
290.0	3.0e-22	3.27	4.46	5.0e+09	5.0e-12	6.8e-12
298.0	2.7e-22	3.07	4.27	5.6e+09	4.6e-12	6.4e-12
300.0	2.6e-22	3.03	4.22	5.7e+09	4.5e-12	6.3e-12
310.0	2.3e-22	2.83	4.02	6.5e+09	4.2e-12	5.9e-12
325.0	1.9e-22	2.60	3.75	7.6e+09	3.7e-12	5.4e-12
ATS2b						
225.0	6.7e-20	454.01	7.66	1.4e+05	4.1e-12	7.0e-14
230.0	5.1e-20	335.89	7.42	2.1e+05	3.6e-12	7.9e-14
240.0	3.1e-20	194.59	6.88	4.6e+05	2.8e-12	9.8e-14
250.0	2.0e-20	119.54	6.42	9.6e+05	2.2e-12	1.2e-13
260.0	1.3e-20	78.84	6.03	1.9e+06	1.9e-12	1.5e-13
270.0	8.7e-21	53.95	5.65	3.5e+06	1.7e-12	1.7e-13
275.0	7.3e-21	45.49	5.49	4.8e+06	1.6e-12	1.9e-13
280.0	6.1e-21	38.74	5.32	6.4e+06	1.5e-12	2.1e-13
290.0	4.4e-21	28.99	5.06	1.1e+07	1.4e-12	2.4e-13
298.0	3.4e-21	23.33	4.81	1.6e+07	1.3e-12	2.7e-13
300.0	3.2e-21	22.25	4.76	1.8e+07	1.3e-12	2.8e-13
310.0	2.4e-21	17.61	4.54	2.9e+07	1.3e-12	3.2e-13

325.0	1.6e-21	13.02	4.20	5.7e+07	1.2e-12	3.9e-13
ATS2c						
225.0	2.9e-22	7.16	6.22	2.8e+09	5.9e-12	5.1e-12
230.0	2.6e-22	6.59	5.99	3.2e+09	5.5e-12	5.0e-12
240.0	2.2e-22	5.71	5.61	4.0e+09	5.0e-12	4.9e-12
250.0	1.8e-22	5.03	5.23	5.0e+09	4.6e-12	4.8e-12
260.0	1.5e-22	4.47	4.91	6.2e+09	4.2e-12	4.6e-12
270.0	1.3e-22	4.04	4.63	7.4e+09	4.0e-12	4.6e-12
275.0	1.2e-22	3.85	4.50	8.2e+09	3.9e-12	4.5e-12
280.0	1.2e-22	3.68	4.38	8.9e+09	3.8e-12	4.5e-12
290.0	1.0e-22	3.36	4.13	1.0e+10	3.6e-12	4.4e-12
298.0	9.3e-23	3.18	3.98	1.2e+10	3.5e-12	4.4e-12
300.0	9.1e-23	3.12	3.93	1.2e+10	3.5e-12	4.4e-12
310.0	8.2e-23	2.93	3.76	1.4e+10	3.4e-12	4.3e-12
325.0	7.1e-23	2.65	3.50	1.7e+10	3.2e-12	4.3e-12
BTS2a						
225.0	2.3e-20	1.28	3.65	6.5e+10	1.9e-09	5.5e-09
230.0	1.9e-20	1.27	3.54	6.6e+10	1.6e-09	4.5e-09
240.0	1.4e-20	1.24	3.33	6.6e+10	1.1e-09	3.0e-09
250.0	1.0e-20	1.22	3.14	6.6e+10	8.1e-10	2.1e-09
260.0	7.5e-21	1.20	2.99	6.6e+10	6.0e-10	1.5e-09
270.0	5.8e-21	1.19	2.84	6.6e+10	4.5e-10	1.1e-09
275.0	5.1e-21	1.18	2.77	6.6e+10	4.0e-10	9.3e-10
280.0	4.6e-21	1.18	2.71	6.6e+10	3.5e-10	8.1e-10
290.0	3.7e-21	1.16	2.60	6.6e+10	2.8e-10	6.2e-10
298.0	3.1e-21	1.15	2.51	6.5e+10	2.3e-10	5.1e-10
300.0	3.0e-21	1.15	2.50	6.5e+10	2.2e-10	4.9e-10
310.0	2.5e-21	1.14	2.40	6.5e+10	1.8e-10	3.8e-10
325.0	1.9e-21	1.13	2.28	6.5e+10	1.4e-10	2.8e-10
BTS2b						
225.0	2.3e-20	1.25	3.83	7.8e+10	2.3e-09	7.0e-09
230.0	1.9e-20	1.24	3.72	7.9e+10	1.9e-09	5.6e-09
240.0	1.4e-20	1.22	3.49	7.9e+10	1.3e-09	3.7e-09
250.0	1.0e-20	1.20	3.30	7.8e+10	9.4e-10	2.6e-09
260.0	7.5e-21	1.19	3.12	7.8e+10	7.0e-10	1.8e-09
270.0	5.8e-21	1.17	2.97	7.8e+10	5.3e-10	1.3e-09
275.0	5.1e-21	1.16	2.90	7.8e+10	4.7e-10	1.2e-09
280.0	4.6e-21	1.16	2.83	7.8e+10	4.1e-10	1.0e-09
290.0	3.7e-21	1.15	2.70	7.7e+10	3.2e-10	7.6e-10
298.0	3.1e-21	1.14	2.61	7.7e+10	2.7e-10	6.2e-10
300.0	3.0e-21	1.14	2.59	7.7e+10	2.6e-10	5.9e-10
310.0	2.5e-21	1.13	2.50	7.6e+10	2.1e-10	4.7e-10
325.0	1.9e-21	1.12	2.36	7.6e+10	1.6e-10	3.4e-10
BTS2c						
225.0	2.3e-20	18.02	6.27	6.2e+07	2.6e-11	8.9e-12
230.0	1.9e-20	15.82	6.04	7.5e+07	2.3e-11	8.7e-12
240.0	1.4e-20	12.66	5.62	1.1e+08	1.9e-11	8.4e-12
250.0	1.0e-20	10.26	5.25	1.5e+08	1.6e-11	8.1e-12

260.0	7.5e-21	8.62	4.95	2.1e+08	1.4e-11	7.8e-12
270.0	5.8e-21	7.34	4.65	2.8e+08	1.2e-11	7.6e-12
275.0	5.1e-21	6.84	4.52	3.2e+08	1.1e-11	7.5e-12
280.0	4.6e-21	6.37	4.39	3.7e+08	1.1e-11	7.4e-12
290.0	3.7e-21	5.60	4.17	4.8e+08	9.7e-12	7.2e-12
298.0	3.1e-21	5.09	3.99	5.7e+08	9.1e-12	7.1e-12
300.0	3.0e-21	4.98	3.96	6.0e+08	8.9e-12	7.1e-12
310.0	2.5e-21	4.49	3.77	7.5e+08	8.3e-12	7.0e-12
325.0	1.9e-21	3.92	3.53	1.0e+09	7.5e-12	6.8e-12

Table S10: Pseudo first order rate constant (k'_{pseudo} in s^{-1}),[a] thermal rate constant ($k_{thermal}$, in s^{-1}),[b] and estimated lifetimes (τ in hours), for atmospheric decomposition of CH_3OOOH. [c]

T (K)	k'_{pseudo} (s^{-1})	$k_{thermal}$ (s^{-1})	τ (hours)
225.0	1.5e-04	3.2e-10	1.8
230.0	1.4e-04	1.1e-09	2.0
240.0	1.1e-04	9.9e-09	2.5
250.0	9.2e-05	7.8e-08	3.0
260.0	7.8e-05	5.3e-07	3.5
270.0	6.8e-05	3.1e-06	3.9
275.0	6.4e-05	7.1e-06	3.9
280.0	6.0e-05	1.6e-05	3.7
290.0	5.3e-05	7.3e-05	2.2
298.0	4.9e-05	2.3e-04	1.0
300.0	4.9e-05	3.1e-04	0.8
310.0	4.4e-05	1.2e-03	0.2
325.0	4.0e-05	7.4e-03	0.0

a) k'_{pseudo} corresponds to the pseudo first order rate constants determined as $k_{TOTAL\text{-}IVTST}$ of the CH_3OOOH+OH reaction, as displayed in table S5 ,times the standard atmospheric concentration of hydroxyl radicals [OH] of 1 x 10^6 molecules·cm^{-3}.
b) Rate constant for the thermal decomposition of CH_3OOOH according the k(i), thermal = 1.1x10^{14} x (T/298) x exp(-12130/T) expression estimated by Müller and co-workers.[6]
c) Lifetime of CH3OOOH at different temperatures computed as 1/($k_{(decomp)}$, where $k_{(decomp)}$ = k'_{pseudo} x $k_{thermal}$

Table S11: Computed harmonic frequencies (in cm-1) for the stationary points of the CH_3O_3H + OH reaction

***cis*-CH_3O_3H**	***trans*-CH_3O_3H**
129.0	155.4
224.0	208.4
352.1	385.8
471.5	466.7
589.0	606.6
946.3	940.6
1005.6	1008.2
1112.0	1103.4
1217.6	1222.1
1264.8	1265.8
1466.1	1481.3
1511.2	1510.6
1536.7	1529.2
1560.5	1564.4
3113.2	3127.2
3183.9	3205.0
3222.3	3223.9
3927.8	3916.5

ACR1a	**ACR2a**	**ACR3a**	**ACP1a**	**ACP2a**	**ACP2b**	**ACP2c**
67.9	29.7	41.2	19.8	53.1	27.8	27.6
128.4	58.8	56.9	45.5	90.2	59.5	54.0
160.2	130.5	125.6	64.0	137.0	74.4	88.5
187.4	177.4	163.7	114.6	157.0	95.2	98.4
210.2	216.1	217.5	133.4	197.4	106.4	130.6
294.2	342.8	323.1	202.7	221.7	147.4	154.1
448.5	363.2	385.7	270.9	289.1	209.9	208.3
502.3	468.6	442.3	347.2	392.9	233.8	374.9
585.8	507.1	470.1	416.9	475.7	236.8	400.6
649.0	599.6	604.5	566.6	550.0	342.9	486.3
930.2	938.7	940.7	848.9	610.8	430.8	597.0
1016.7	1004.8	1008.9	1082.0	724.8	623.2	609.7

1098.8	1097.6	1096.1	1224.6	908.6	1286.5	929.8
1222.9	1222.0	1223.3	1261.3	1032.7	1296.3	1024.2
1265.8	1266.0	1267.6	1365.2	1196.1	1331.9	1192.7
1510.9	1466.7	1484.2	1511.5	1242.5	1579.7	1245.2
1528.0	1515.2	1513.8	1525.5	1490.9	1621.5	1493.3
1546.7	1534.6	1532.0	1565.0	1605.3	1682.1	1498.9
1565.2	1562.1	1565.5	1684.0	1685.7	1860.6	1691.2
3133.6	3132.1	3132.0	3128.5	3237.1	3075.8	3239.6
3216.3	3214.5	3214.5	3207.2	3385.3	3176.1	3389.0
3227.7	3229.9	3230.5	3236.6	3736.8	3634.0	3909.2
3788.4	3811.4	3828.1	3951.4	3954.6	3940.3	3967.2
3817.6	3918.5	3913.5	4070.8	4066.0	4071.6	4072.4

ATS1a	**ATS1b**	**ATS2a**	**ATS2b**	**ATS2c**
-2304.4	-2164.5	-1835.0	-1982.7	-1752.2
60.0	75.7	93.1	18.5	52.6
105.1	100.4	136.5	97.0	110.2
179.5	134.6	177.8	121.2	152.7
211.2	203.5	304.1	151.1	198.9
241.4	218.4	388.9	353.4	397.2
443.0	449.3	431.1	396.5	407.3
472.3	471.8	482.0	437.6	470.9
621.4	623.4	593.9	573.0	603.6
772.2	746.7	646.4	691.6	662.1
934.0	936.2	897.4	812.8	888.7
1065.8	1067.6	937.7	936.3	936.5
1103.3	1108.6	1018.4	1025.9	1020.9
1221.0	1220.6	1138.9	1120.9	1138.1
1238.5	1262.8	1193.8	1171.2	1180.8
1264.4	1285.7	1268.5	1249.0	1274.4
1433.6	1368.6	1351.6	1266.3	1365.6
1510.7	1510.7	1484.9	1489.6	1487.1
1529.6	1529.7	1498.6	1516.3	1495.5

1564.2	1563.5	1535.3	1545.8	1516.9
3129.9	3127.9	3165.7	3155.3	3167.1
3210.3	3206.8	3263.6	3252.1	3262.3
3228.1	3228.1	3911.1	3911.2	3910.6
3916.2	3928.4	3915.6	3925.7	3923.3

BCR1a	**BCP2a**	**BCP2b**	**BCP2c**
26.8	66.7	67.2	56.5
59.5	111.1	118.5	70.8
102.0	120.5	118.9	84.2
135.0	178.8	191.6	106.6
192.9	223.5	230.8	133.8
227.4	292.4	256.2	173.8
292.8	346.0	312.4	197.7
458.7	422.8	420.8	218.6
590.8	507.0	508.5	243.2
594.0	545.7	540.6	409.8
947.0	757.9	779.9	534.4
1009.9	774.8	806.0	726.1
1110.9	909.8	908.4	1300.5
1216.1	1053.3	1056.5	1317.4
1264.7	1219.0	1220.0	1338.5
1503.4	1265.0	1266.5	1595.9
1518.5	1496.2	1496.7	1643.9
1535.6	1631.4	1611.9	1708.7
1558.7	1675.7	1683.4	1868.7
3115.2	3212.0	3210.4	3050.2
3186.4	3352.0	3349.7	3170.5
3221.1	3700.4	3693.1	3527.9
3845.2	3911.1	3914.4	3860.4
3866.4	4048.8	4051.0	4057.6

BTS1a	**BTS1b**	**BTS2a**	**BTS2b**	**BTS2c**

-1974.8	-1821.5	-1248.1	-1289.5	-1756.8
47.3	62.6	127.3	128.2	37.5
104.0	104.3	179.0	184.1	96.0
190.3	156.9	188.6	199.0	161.8
201.9	210.1	298.6	289.5	193.7
212.0	212.7	385.6	391.0	387.6
372.0	426.1	476.5	467.3	401.7
477.2	490.9	569.9	567.4	468.0
580.5	583.2	665.6	709.1	590.5
773.2	740.8	734.1	743.6	662.1
944.1	938.6	905.1	869.0	846.1
1069.4	1070.0	931.7	923.0	939.6
1086.6	1093.0	1041.9	1043.1	1017.5
1186.7	1222.4	1156.1	1155.7	1146.3
1223.5	1236.4	1210.7	1261.6	1212.1
1265.0	1265.9	1296.5	1334.2	1268.1
1513.3	1500.3	1396.8	1397.0	1330.9
1529.8	1516.7	1491.0	1480.8	1476.8
1566.2	1533.4	1536.0	1521.5	1513.7
1615.5	1564.9	1599.8	1593.8	1534.1
3128.3	3126.7	3146.7	3147.5	3151.9
3207.5	3205.2	3248.2	3246.1	3255.4
3226.0	3226.6	3753.8	3740.6	3918.5
3918.6	3922.6	3916.2	3923.5	3923.4

Table. S12. Cartesian Coordinates (in Angstroms) of the stationary points optimized.

Geometries optimized at BH&HLYP/6-311+G(2df,2p)

OH

O	0.000000	0.000000	0.106843
H	0.000000	0.000000	-0.854742

trans-CH3OOOH

O	0.605776	-0.514401	0.405261
O	1.413136	0.519184	-0.058279
O	-0.529519	-0.552438	-0.390524
H	1.875002	0.115077	-0.791227

C	-1.451121	0.398235	0.092709
H	-2.316336	0.300024	-0.547346
H	-1.720595	0.178307	1.117526
H	-1.046489	1.398425	0.013127

RTS2

O	0.591581	-0.554062	0.353066
O	1.394704	0.490541	-0.194492
O	-0.550535	-0.544535	-0.394590
H	2.166997	0.416789	0.362902
C	-1.438658	0.417950	0.132252
H	-2.325430	0.339133	-0.479820
H	-1.676525	0.189836	1.163144
H	-1.019099	1.410991	0.048391

RTS4

O	0.290696	-0.641139	-0.038963
O	-0.251652	0.217850	0.890723
O	1.387280	-0.042904	-0.748276
H	0.160525	-0.055188	1.708367
C	1.768381	1.222766	-0.290467
H	2.580579	1.479812	-0.956668
H	0.977154	1.953093	-0.384577
H	2.142028	1.204333	0.726835

RTS3

O	0.038591	-0.001196	-0.087558
O	0.085445	-0.057124	1.295700
O	1.368147	0.139060	-0.542501
C	-0.181788	-1.388121	1.685913
H	1.886818	-0.088298	0.227953
H	-0.142440	-1.375596	2.765815
H	-1.166581	-1.689688	1.356293
H	0.565563	-2.067785	1.295106

RTS1

O	-0.013693	-0.094782	0.001004
O	-0.031777	0.039699	1.364097
O	1.359066	-0.070054	-0.362915
H	0.142455	-0.845349	1.682480
C	1.432043	-0.761147	-1.580246
H	2.473393	-0.712863	-1.865039
H	1.127040	-1.794806	-1.464425
H	0.827984	-0.279739	-2.340513

cis-CH3OOOH

O	-0.613488	-0.523415	0.391744
O	-1.471898	0.392577	-0.213776
O	0.550634	-0.577094	-0.356059
H	-1.375499	1.173539	0.327461

C	1.436275	0.418267	0.090987
H	2.343015	0.263666	-0.475992
H	1.053382	1.410205	-0.121433
H	1.639467	0.306441	1.148769

H2CO

C	0.000000	0.000000	-0.520956
O	0.000000	0.000000	0.665681
H	0.000000	0.930143	-1.099855
H	0.000000	-0.930143	-1.099855

OOH

O	0.054271	-0.597052	0.000000
O	0.054271	0.704958	0.000000
H	-0.868342	-0.863251	0.000000

O2

O	0.000000	0.000000	0.589830
O	0.000000	0.000000	-0.589830

CH3O

C	-0.004560	-0.028291	-0.065000
O	-0.097068	0.030105	1.293591
H	1.024073	0.012273	-0.414381
H	-0.528821	-0.884721	-0.481521
H	-0.507965	0.870633	-0.431992

ACR3a

C	-0.152265	-1.395081	-0.830488
O	-0.255111	-1.083175	0.544324
H	0.860455	-1.246199	-1.179575
H	-0.412104	-2.441813	-0.892650
H	-0.848838	-0.803096	-1.408919
O	-1.306274	2.088496	-1.256203
H	-0.822638	1.620344	-0.564920
O	0.030925	0.260501	0.728319
O	1.413131	0.412006	0.753105
H	1.632390	0.204124	1.660533

ATS2c

C	0.020837	0.031777	0.028333
O	0.020218	0.019861	1.408941
H	1.007151	0.160476	-0.393524
H	-0.481571	-0.865477	-0.298867
H	-0.659597	0.958942	-0.386038
O	-1.287309	2.027655	-0.723337
H	-0.898415	2.629524	-0.087387
O	0.669429	1.159669	1.876251
O	2.033639	0.914067	1.839544

H	2.191274	0.452467	2.662376

ACP2c

C	-0.050092	-1.575289	-0.721948
O	0.021934	-1.322584	0.611749
H	0.313930	-0.823960	-1.393191
H	-0.004456	-2.625832	-0.923782
H	-2.027385	1.622916	-1.630091
O	-1.089947	1.735111	-1.534184
H	-0.862528	1.320708	-0.708411
O	0.011471	0.050581	0.845953
O	1.322720	0.494267	0.789190
H	1.647396	0.321474	1.672452

ACR2a

O	-1.174102	-0.049572	0.438857
O	-0.540810	-1.119221	-0.190371
O	-0.917011	1.089561	-0.303072
H	-1.148313	-1.358726	-0.888671
C	0.294241	1.664836	0.143567
H	0.405350	2.562620	-0.447179
H	0.226335	1.917518	1.193162
H	1.129707	1.001430	-0.033904
O	2.335581	-1.496891	0.218924
H	1.372862	-1.482364	0.143614

ATS2a

O	-1.313561	-0.008817	0.362269
O	-0.896135	-1.276476	-0.021072
O	-0.652103	0.913802	-0.441139
H	-1.450056	-1.468797	-0.776867
C	0.548829	1.260761	0.147676
H	0.962009	2.072864	-0.430536
H	0.451925	1.471798	1.202705
H	1.368898	0.350454	0.052300
O	2.097239	-0.692901	-0.018169
H	1.383678	-1.332250	0.015254

ACP2a

O	-0.881634	-0.047040	-0.342714
O	-0.615675	-0.907433	0.704800
O	0.069730	0.982937	-0.307634
H	0.123343	-1.423487	0.358038
C	-0.315218	1.948628	0.559524
H	0.386454	2.756265	0.603796
H	-1.366507	2.062460	0.731113
H	2.528868	-1.803221	-0.452600
O	1.657424	-1.559096	-0.739811

H	1.692964	-0.633629	-0.963975

ACR1a

O	0.607640	0.578176	-0.483307
O	1.134363	0.412939	0.789217
O	-0.570958	-0.163290	-0.557760
H	0.604862	1.024505	1.310074
C	-0.249405	-1.511714	-0.824701
H	0.278534	-1.589681	-1.765356
H	0.341383	-1.926340	-0.019750
H	-1.199863	-2.022004	-0.887819
O	-1.347722	1.708331	1.483731
H	-1.533123	1.128154	0.732445

ATS2b

O	1.452138	0.333046	-0.506012
O	2.119346	-0.278116	0.542963
O	0.118757	0.513148	-0.113122
H	2.341265	0.455756	1.114707
C	-0.574339	-0.665154	-0.351186
H	-0.606271	-0.931780	-1.397390
H	-0.293784	-1.468490	0.314358
H	-1.746544	-0.388010	-0.040849
O	-2.853791	0.074853	0.280404
H	-2.626517	1.003500	0.342412

ACP2b

O	2.815303	-0.636248	0.111702
O	2.418084	0.302619	0.920076
O	-0.227994	-0.013244	0.216951
H	1.454719	0.339537	0.804937
C	-0.366510	-0.873328	-0.606106
H	-1.357191	-1.118754	-0.987193
H	0.492449	-1.424234	-0.987568
H	-2.233276	0.582270	0.461329
O	-3.069858	0.321036	0.086414
H	-3.733608	0.861481	0.494834

BCR1a

O	-0.513180	-0.512749	0.503306
O	-0.451045	-1.034384	-0.786561
O	-1.007857	0.779904	0.423994
H	0.486261	-0.976402	-0.984107
C	0.042260	1.670532	0.142828
H	-0.412855	2.650582	0.150554
H	0.809609	1.618684	0.906352
H	0.466452	1.482951	-0.835914
O	2.337673	-0.790073	-0.105971
H	2.043330	-1.184507	0.722437

BTS2a

O	-1.192415	-0.267864	0.411575
O	-0.704469	-1.415237	-0.182187
O	-0.844930	0.810196	-0.414796
H	0.233450	-1.401457	0.042312
C	0.274266	1.405758	0.107840
H	0.530049	2.242553	-0.524331
H	0.176006	1.664441	1.154807
H	1.180489	0.627266	0.096498
O	1.972158	-0.487892	0.099701
H	2.322261	-0.411749	-0.789562

BCP2a

O	-1.054058	-0.237444	0.454894
O	-0.574219	-1.323801	-0.237645
O	-0.928907	0.884779	-0.388005
H	0.379622	-1.284487	-0.082241
C	0.032252	1.698054	0.085433
H	0.086816	2.612244	-0.473136
H	0.222924	1.666473	1.142303
H	1.986640	0.227351	-0.047666
O	2.117356	-0.703196	0.120990
H	2.811801	-0.993212	-0.458837

BTS2b

O	-0.016678	0.037529	0.004460
O	-0.000246	-0.008940	1.384124
O	1.317764	0.002208	-0.425442
H	0.235976	0.893671	1.630929
C	1.692537	1.277679	-0.759764
H	2.724120	1.247803	-1.077471
H	1.030222	1.746316	-1.476260
H	1.648285	1.952459	0.228791
O	1.225490	2.533103	1.390693
H	0.751640	3.280430	1.023167

BCP2b

O	-0.825115	-0.707083	-0.357380
O	-0.767923	-0.740720	1.014753
O	0.490629	-0.896408	-0.830881
H	-0.513714	0.162906	1.249329
C	0.910497	0.222821	-1.445885
H	1.879433	0.090267	-1.886753
H	0.160283	0.838459	-1.907179
H	0.797454	1.766844	0.487210
O	0.272139	1.814146	1.282875
H	-0.207649	2.633212	1.247600

BTS2c

O	-0.878373	-0.647900	0.349154
O	-1.939049	-0.069010	-0.335692
O	-0.273611	0.334956	1.125601
H	-1.599741	0.023455	-1.224545
C	0.577309	1.096434	0.356534
H	0.089722	1.590331	-0.473995
H	1.076515	1.784064	1.021097
H	1.451468	0.400457	-0.141288
O	2.257105	-0.442863	-0.682945
H	1.841776	-1.253366	-0.385251

BCP2c

O	-0.642530	-1.683553	-0.949753
O	-1.657568	-0.912828	-0.716848
O	-0.766602	1.469364	0.231751
H	-1.301340	-0.068574	-0.378571
C	0.307905	1.940454	0.468364
H	1.225673	1.378038	0.305848
H	0.385225	2.958473	0.857376
H	2.685789	-1.158994	-0.568001
O	1.966249	-0.569128	-0.383658
H	1.162363	-1.039828	-0.605537

ATS1a

O	0.179902	0.634717	-0.650164
O	-0.630706	0.883639	0.396488
O	0.884038	-0.539016	-0.388521
H	-1.551967	0.386291	0.164195
C	1.986905	-0.234523	0.438314
H	2.495263	-1.177411	0.579299
H	2.643574	0.471657	-0.052268
H	1.654839	0.150851	1.392860
O	-2.413571	-0.542428	0.025267
H	-1.897092	-1.349454	-0.017803

ACP1a

O	0.858722	1.571396	-0.384735
O	-0.073341	2.182724	-0.926164
O	0.562703	0.158732	-0.375322
H	-2.441420	-1.524709	0.674480
C	1.584346	-0.451495	0.380497
H	1.305595	-1.494415	0.411139
H	2.544625	-0.333361	-0.104256
H	1.608369	-0.054877	1.386857
O	-1.524968	-1.398614	0.884604
H	-1.219270	-0.683604	0.334478

ATS1b

O	-0.647134	0.177034	-0.534693

O	-0.625672	0.217007	0.812779
O	0.661980	0.230640	-1.004330
H	-0.308326	-0.745919	1.134887
C	1.078706	1.578491	-1.029270
H	2.083473	1.547758	-1.425175
H	0.440523	2.161979	-1.680000
H	1.090319	1.995556	-0.031161
O	-0.329074	-1.973848	1.534196
H	-1.230523	-2.273226	1.407193

BTS1a

O	-0.634488	0.737626	-0.374809
O	-0.585340	0.745804	1.016885
O	0.627818	0.718757	-0.846717
C	-0.909621	-0.549501	1.476056
H	-1.904593	-0.830349	1.155904
H	-0.185228	-1.277007	1.135967
H	-0.880221	-0.471062	2.553521
H	0.815131	-0.270880	-1.139271
O	1.272599	-1.514642	-1.091192
H	2.149055	-1.446207	-0.708119

BTS1b

C	-0.168555	1.498091	-1.005487
O	-0.376133	1.299595	0.376796
H	0.852344	1.800886	-1.198921
H	-0.844780	2.298669	-1.268795
H	-0.412212	0.608874	-1.571846
O	0.516831	0.328679	0.825671
O	-0.144144	-0.839210	0.949483
H	-0.181621	-1.272166	-0.001494
O	0.112057	-1.975425	-1.091764
H	0.874137	-2.508718	-0.859516

CH2OOOH

C	-1.085556	0.677204	-0.951380
O	-0.658087	0.459665	0.316763
H	-0.506916	0.253732	-1.747365
H	-1.612239	1.605783	-1.037000
O	0.016724	-0.758374	0.392301
O	1.341851	-0.516224	0.069798
H	1.715448	-0.216595	0.897783

CTS1

C	-0.976171	0.813193	-0.963471
O	-0.519925	0.648683	0.283622
H	-0.420487	0.397108	-1.778129
H	-1.909432	1.329283	-1.052844
O	-0.020426	-0.679686	0.460040

O	1.310568	-0.662827	0.102002
H	1.747097	-0.340564	0.889680

CCP1

C	-0.844827	0.973795	-1.032042
O	0.317576	1.108344	-0.796373
H	-1.371905	1.682163	-1.674974
H	-1.417755	0.144212	-0.616376
O	0.114952	-1.449497	0.930565
O	1.275402	-0.866891	0.853491
H	1.130540	-0.098798	0.276479

CTS2

C	0.042689	0.112353	-0.005136
O	0.090691	-0.037663	1.307402
H	0.850944	-0.264232	-0.594530
H	-0.845793	0.587396	-0.358374
O	1.228715	-0.502581	1.762392
O	2.342142	0.810980	1.839494
H	2.215285	0.960146	2.775492

CCP2

C	-0.795608	0.095377	-1.085129
O	-1.078085	-0.334443	0.022138
H	0.199813	-0.030934	-1.474022
H	-1.588441	0.591393	-1.617343
O	-0.086530	-0.959112	0.738267
O	1.577623	1.162662	0.454488
H	1.112877	0.362710	0.776511

cis-CH3OOO

C	1.297801	0.406534	0.000000
O	0.000000	0.936411	0.000000
H	1.915131	1.293971	0.000000
H	1.496473	-0.179975	0.886898
H	1.496473	-0.179975	-0.886898
O	-1.016255	-0.101154	0.000000
O	-0.570605	-1.256910	0.000000

DTS1

C	-0.023319	-0.065137	0.057934
O	0.110554	0.069869	1.430211
H	0.957308	0.207055	-0.318257
H	-0.759616	0.613813	-0.357151
H	-0.243663	-1.083834	-0.240572
O	-1.302241	-0.310435	2.128874
O	-2.168295	-0.627192	1.350569

trans-CH3OOO

O	-0.240186	-0.727376	0.000000

O	0.000000	0.695641	0.000000
O	-1.461265	-0.940493	0.000000
C	1.396876	0.841889	0.000000
H	1.836540	0.408076	0.889648
H	1.836540	0.408076	-0.889648
H	1.557271	1.910334	0.000000

DTS2

C	1.650633	-0.185408	0.000041
O	0.506330	0.606421	-0.000043
H	2.474567	0.519628	-0.000248
H	1.717375	-0.800573	0.890668
H	1.717170	-0.801027	-0.890287
O	-0.714735	-0.457256	-0.000062
O	-1.768208	0.125138	0.000058

Geometries optimized at CASSCF(11,10)

CH2OOOH

C	1.3988733187	0.6349696212	0.0880453771
O	0.6126945801	-0.4042801410	-0.3958269795
O	-0.5419215836	-0.5230572280	0.4344411941
H	1.3563141738	0.8069579612	1.1436499493
H	2.3183784903	0.6878355177	-0.4576950683
O	-1.5224857505	0.4389389782	-0.0745723954
H	-1.9055761901	-0.0775030836	-0.7997322129

CTS2

C	1.4621771036	0.6028158690	0.0898356385
O	0.7029459119	-0.4138416526	-0.3907511045
O	-0.3837781782	-0.6607547354	0.3623058305
H	1.2651584070	0.9536166041	1.0775646714
H	2.3713403624	0.7285929479	-0.4532319565
O	-1.7022036175	0.5907581523	-0.1414023281
H	-2.1401430586	-0.0807853343	-0.6897756911

CCP2

C	1.2966736147	0.5303773972	0.0341225555
O	0.9128247183	-0.6034209309	-0.3373394491
O	-0.1680978073	-1.1540250911	0.3662712613
H	0.8015310881	1.0215275862	0.8471168025
H	2.1226690974	0.9403632073	-0.5113705885
O	-1.9289518651	0.9918280681	-0.4591892054
H	-1.5841845234	0.1155948183	-0.1896234463

CTS1

C	1.5413248806	0.4277223747	-0.0503935125
O	0.6467052943	-0.4909023756	-0.5112780088
O	-0.5028968829	-0.5940998947	0.4594313231
H	1.1567292693	1.3061135240	0.4209856847
H	2.5380445415	0.0686412708	0.1022850644

O	-1.4475298140	0.4244506135	0.0396609047
H	-1.8819275992	-0.0307201736	-0.6972048891

CCP1

C	1.6758066029	0.3474485889	-0.1244886414
O	0.9173101151	0.0081628662	-1.0155190860
O	-1.6162767696	0.1839165180	1.0623031381
H	1.3103614271	0.5560137150	0.8750952962
H	2.7400983471	0.4491039800	-0.3117220783
O	-1.9115239704	-0.1886929775	-0.1979336411
H	-1.0400820569	-0.1751186683	-0.6358572585

Geometries optimized at CCSD(T)/6-311+G(2df,2p)

cis-CH3OOO

C	-1.280160	0.488456	-0.000000
O	-0.638052	-0.768269	0.000000
H	-2.336491	0.219605	0.000000
H	-1.044619	1.068280	0.894090
H	-1.044619	1.068280	-0.894090
O	0.879343	-0.545096	-0.000000
O	1.220121	0.657861	0.000000

tramns-CH3OOO

O	0.647673	-0.455669	-0.000000
O	-0.438424	0.600028	-0.000000
O	1.769412	0.094821	0.000000
C	-1.640443	-0.155469	-0.000000
H	-1.720495	-0.771950	-0.897311
H	-1.720495	-0.771950	0.897311
H	-2.431357	0.593601	0.000000

DTS3

C	0.004799	0.000382	0.003025
O	0.059798	0.033722	1.424061
H	1.048708	-0.004675	-0.309214
H	-0.490869	-0.906699	-0.348673
H	-0.490344	0.888596	-0.393442
O	-1.376491	0.126710	1.857614
O	-1.727297	-0.931917	2.442145

Geometries optimized at CCSD(T)/aug-cc-pVTZ

CH3O

C	-0.002551	-0.031650	-0.067161
O	-0.099362	0.033179	1.306228
H	1.034675	0.013760	-0.418907
H	-0.535089	-0.893002	-0.486816
H	-0.512015	0.877711	-0.432647

O2

O	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.213182

cis-CH3OOO

C	-1.281004	0.490179	-0.000000
O	-0.637982	-0.769980	0.000000
H	-2.338114	0.218683	0.000000
H	-1.043009	1.068594	0.895877
H	-1.043009	1.068594	-0.895877
O	0.879772	-0.547342	-0.000000
O	1.218869	0.660387	0.000000

trans-CH3OOO

O	0.646712	-0.456894	-0.000000
O	-0.437217	0.601789	0.000000
O	1.772643	0.095225	-0.000000
C	-1.642232	-0.155915	0.000000
H	-1.720230	-0.772697	-0.898794
H	-1.720230	-0.772697	0.898794
H	-2.433576	0.594600	-0.000000

DTS2

C	1.681808	-0.173890	-0.002265
O	0.573084	0.687743	0.007783
H	2.553459	0.490893	-0.001062
H	1.723128	-0.800571	0.894772
H	1.715555	-0.791896	-0.905493
O	-0.798847	-0.493239	0.038389
O	-1.865056	0.087883	-0.031999

DTS1

C	0.077875	-0.198696	0.056806
O	0.254710	-0.357399	1.420174
H	0.647318	0.660779	-0.312607
H	-0.991976	0.018953	-0.138327
H	0.326462	-1.114563	-0.489727
O	-1.437376	-0.215606	2.167531
O	-2.306285	0.010672	1.347757

Geometries optimized at QCISD/6-311+G(2df,2p)

cis-CH3OOO

C	1.292335	0.432208	0.000000
O	0.000000	0.993165	0.000000
H	1.938243	1.308374	0.000000
H	1.478663	-0.164055	0.892827
H	1.478663	-0.164055	-0.892827
O	-1.039166	-0.148440	0.000000

O	-0.542031	-1.291413	0.000000

trans-CH3OOO

O	-0.240462	-0.735636	0.000000
O	0.000000	0.720906	0.000000
O	-1.480363	-0.951480	0.000000
C	1.413591	0.838930	0.000000
H	1.844146	0.392672	0.896037
H	1.844146	0.392672	-0.896037
H	1.596762	1.910753	0.000000

DTS1

6	-0.054843	-0.307101	0.030207
8	0.014434	-0.816932	1.327866
1	0.067563	0.777645	-0.000048
1	-0.974384	-0.595248	-0.483564
1	0.792914	-0.771631	-0.477480
8	-1.299406	-0.118253	2.170540
8	-1.975552	0.635659	1.484088

DTS2

6	1.665806	-0.178938	0.000108
8	0.533661	0.651627	-0.000132
1	2.516177	0.505260	-0.000039
1	1.715076	-0.800133	0.896549
1	1.715154	-0.800533	-0.896056
8	-0.746766	-0.478743	0.000037
8	-1.815977	0.108385	-0.000342

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