Supporting Information for

Improved Computational Modeling of the Kinetics of the Acetylperoxy + HO_2 Reaction

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Supplementary Figures

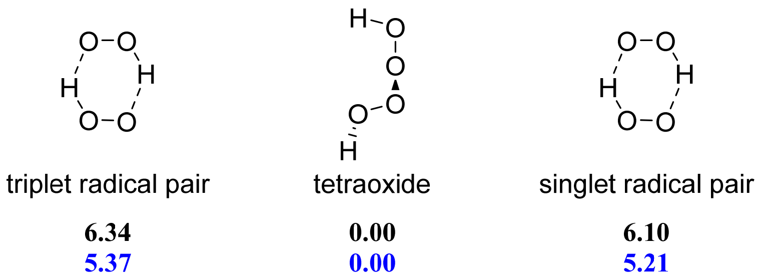

Figure S1. Relative energies (0 K, kcal mol^{-1}) for structures in the HO_2 + HO_2 system. Values in black from the CCSD(T)/CBS//CCSD(T)/cc-pVTZ and MRCI(2,2)+Q-F12/VTZ-F12//CCSD(T)/cc-pVTZ calculations of Sprague and Irikura.[1] Values in blue from (U)W1BD calculations from this work.

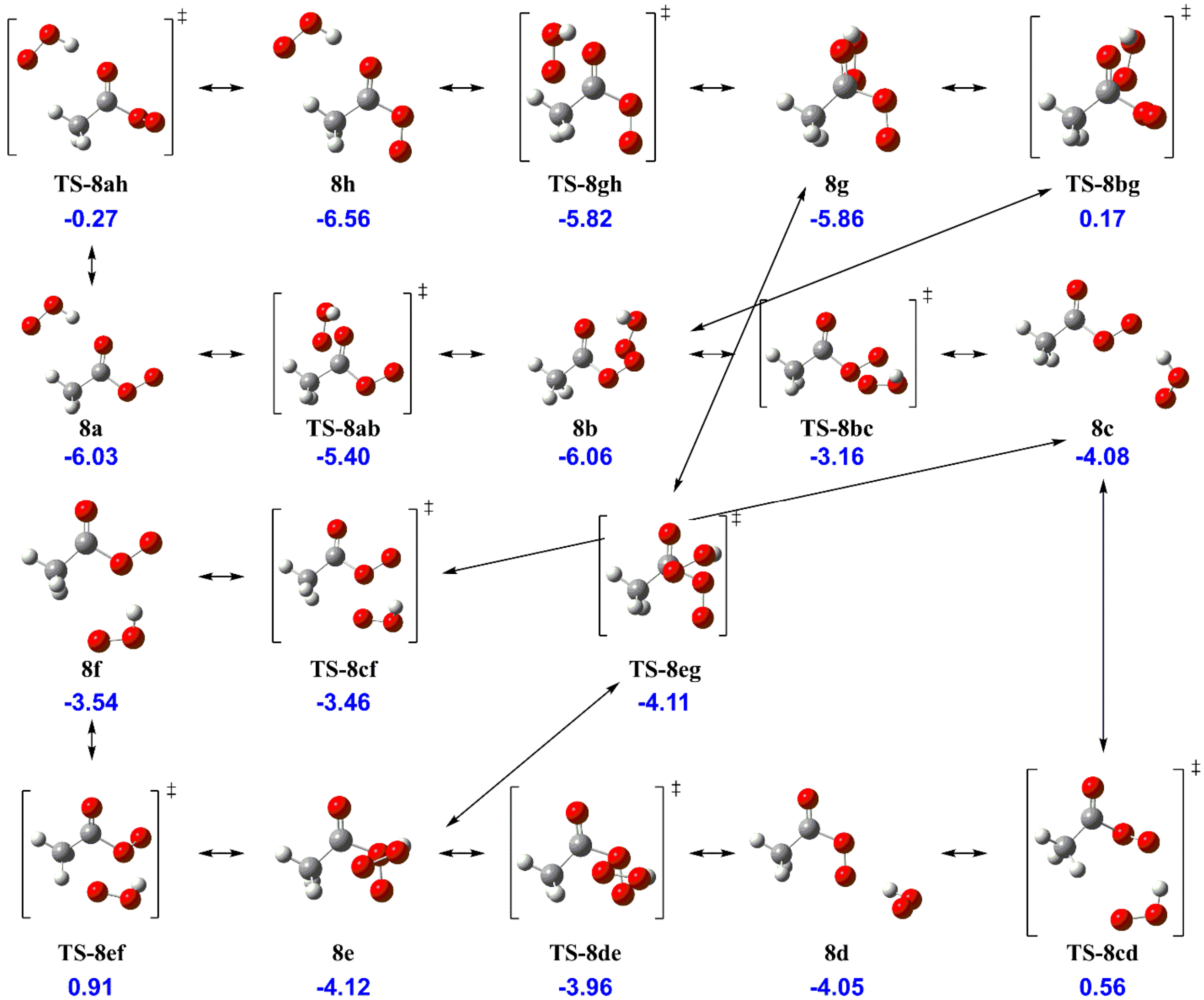

Figure S2. Singlet pre-reactive complexes and interconversion transition structures for the acetylperoxy + HO_2 reaction. Energies (0 K, kcal mol^{-1}) in blue from UW1BD//B3LYP calculations relative to the combined energies of *anti* acetylperoxy + HO_2.

Supplementary Tables

TABLE 1S: RRKM/ME Yields and Triplet Rate Coefficients at 230 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9837	1.08×10^{-4}	0.01619	1.2×10^{-7}	2.96×10^{-11}
10	0.9837	1.08×10^{-4}	0.01622	1.5×10^{-7}	2.96×10^{-11}
20	0.9837	1.06×10^{-4}	0.01624	1.6×10^{-7}	2.96×10^{-11}
30	0.9836	1.06×10^{-4}	0.01626	1.8×10^{-7}	2.98×10^{-11}
40	0.9836	1.08×10^{-4}	0.01627	2.0×10^{-7}	2.98×10^{-11}
50	0.9836	1.08×10^{-4}	0.01632	1.4×10^{-7}	2.98×10^{-11}
100	0.9835	1.07×10^{-4}	0.01639	1.3×10^{-7}	3.00×10^{-11}
200	0.9833	1.06×10^{-4}	0.01661	1.5×10^{-7}	3.03×10^{-11}
300	0.9831	1.05×10^{-4}	0.01679	1.6×10^{-7}	3.07×10^{-11}
400	0.9829	1.07×10^{-4}	0.01699	7×10^{-8}	3.11×10^{-11}
500	0.9827	1.07×10^{-4}	0.01718	1.8×10^{-7}	3.14×10^{-11}
600	0.9825	1.07×10^{-4}	0.01735	1.3×10^{-7}	3.18×10^{-11}
700	0.9824	1.07×10^{-4}	0.01754	8×10^{-8}	3.20×10^{-11}
760	0.9822	1.07×10^{-4}	0.01765	2.2×10^{-7}	3.23×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 2S: RRKM/ME Yields and Triplet Rate Coefficients at 230 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	3.91×10^{-5}	0	8.7×10^{-7}	9×10^{-14}
10	1.0000	3.91×10^{-5}	1×10^{-8}	6.9×10^{-7}	9×10^{-14}
20	1.0000	4.01×10^{-5}	0	6.8×10^{-7}	9×10^{-14}
30	1.0000	3.91×10^{-5}	1×10^{-8}	7.7×10^{-7}	9×10^{-14}
40	1.0000	3.89×10^{-5}	0	5.6×10^{-7}	9×10^{-14}
50	1.0000	3.89×10^{-5}	0	6.5×10^{-7}	9×10^{-14}
100	1.0000	3.93×10^{-5}	2×10^{-8}	$.8.4 \times 10^{-7}$	9×10^{-14}
200	1.0000	3.91×10^{-5}	0	7.5×10^{-7}	9×10^{-14}
300	1.0000	3.96×10^{-5}	0	7.2×10^{-7}	9×10^{-14}
400	1.0000	3.84×10^{-5}	0	7.4×10^{-7}	9×10^{-14}
500	1.0000	3.79×10^{-5}	0	5.9×10^{-7}	9×10^{-14}
600	1.0000	3.87×10^{-5}	0	8.5×10^{-7}	9×10^{-14}
700	1.0000	3.81×10^{-5}	1×10^{-8}	8.5×10^{-7}	9×10^{-14}
760	1.0000	3.88×10^{-5}	0	8.7×10^{-7}	9×10^{-14}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 3S: RRKM/ME Yields and Triplet Rate Coefficients at 230 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	6.97 x 10^{-5}	0.9998	6.7 x 10^{-6}	7.44 x 10^{-5}	2.2 x 10^{-13}
10	6.99 x 10^{-5}	0.9999	6.5 x 10^{-6}	7.32 x 10^{-5}	5.1 x 10^{-14}
20	7.03 x 10^{-5}	0.9999	7.0 x 10^{-6}	7.27 x 10^{-5}	5.0 x 10^{-14}
30	6.93 x 10^{-5}	0.9999	6.0 x 10^{-6}	7.27 x 10^{-5}	5.2 x 10^{-14}
40	7.02 x 10^{-5}	0.9999	6.3 x 10^{-6}	7.30 x 10^{-5}	5.0 x 10^{-14}
50	7.19 x 10^{-5}	0.9998	6.5 x 10^{-6}	7.45 x 10^{-5}	2.2 x 10^{-13}
100	6.97 x 10^{-5}	0.9998	6.8 x 10^{-6}	7.44 x 10^{-5}	2.2 x 10^{-13}
200	6.93 x 10^{-5}	0.9999	6.5 x 10^{-6}	7.37 x 10^{-5}	5.2 x 10^{-14}
300	6.92 x 10^{-5}	0.9999	6.6 x 10^{-6}	7.33 x 10^{-5}	5.2 x 10^{-14}
400	7.13 x 10^{-5}	0.9998	6.9 x 10^{-6}	7.36 x 10^{-5}	2.2 x 10^{-13}
500	6.98 x 10^{-5}	0.9999	6.3 x 10^{-6}	7.31 x 10^{-5}	5.1 x 10^{-14}
600	6.91 x 10^{-5}	0.9999	6.4 x 10^{-6}	7.17 x 10^{-5}	5.2 x 10^{-14}
700	6.97 x 10^{-5}	0.9998	6.6 x 10^{-6}	7.41 x 10^{-5}	2.2 x 10^{-13}
760	7.16 x 10^{-5}	0.9998	6.7 x 10^{-6}	7.48 x 10^{-5}	2.2 x 10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 4S: RRKM/ME Yields and Triplet Rate Coefficients at 240 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9858	1.040×10^{-4}	0.01411	1.3×10^{-7}	2.58×10^{-11}
10	0.9858	1.047×10^{-4}	0.01412	1.5×10^{-7}	2.58×10^{-11}
20	0.9858	1.034×10^{-4}	0.01414	1.9×10^{-7}	2.58×10^{-11}
30	0.9857	1.034×10^{-4}	0.01416	1.9×10^{-7}	2.59×10^{-11}
40	0.9857	1.043×10^{-4}	0.01415	2.3×10^{-7}	2.59×10^{-11}
50	0.9857	1.037×10^{-4}	0.01419	1.8×10^{-7}	2.59×10^{-11}
100	0.9856	1.039×10^{-4}	0.01426	1.1×10^{-7}	2.61×10^{-11}
200	0.9855	1.032×10^{-4}	0.01443	2.7×10^{-7}	2.63×10^{-11}
300	0.9853	1.032×10^{-4}	0.01458	1.5×10^{-7}	2.67×10^{-11}
400	0.9852	1.040×10^{-4}	0.01471	1.1×10^{-7}	2.69×10^{-11}
500	0.9850	1.033×10^{-4}	0.01489	1.4×10^{-7}	2.72×10^{-11}
600	0.9849	1.035×10^{-4}	0.01503	2.0×10^{-7}	2.74×10^{-11}
700	0.9847	1.039×10^{-4}	0.01516	5.0×10^{-8}	2.78×10^{-11}
760	0.9846	1.047×10^{-4}	0.01525	1.6×10^{-7}	2.80×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 5S: RRKM/ME Yields and Triplet Rate Coefficients at 240 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	4.03 x 10^{-5}	0	9.7 x 10^{-7}	2 x 10^{-15}
10	1.0000	4.03 x 10^{-5}	1 x 10^{-8}	8.2 x 10^{-7}	2 x 10^{-15}
20	1.0000	4.12 x 10^{-5}	2 x 10^{-8}	7.4 x 10^{-7}	1 x 10^{-15}
30	1.0000	4.02 x 10^{-5}	1 x 10^{-8}	8.5 x 10^{-7}	2 x 10^{-15}
40	1.0000	3.96 x 10^{-5}	1 x 10^{-8}	9.5 x 10^{-7}	2 x 10^{-15}
50	1.0000	4.09 x 10^{-5}	1 x 10^{-8}	8.2 x 10^{-7}	2 x 10^{-15}
100	1.0000	4.02 x 10^{-5}	1 x 10^{-8}	8.4 x 10^{-7}	2 x 10^{-15}
200	1.0000	4.11 x 10^{-5}	2 x 10^{-8}	7.8 x 10^{-7}	1 x 10^{-15}
300	1.0000	4.10 x 10^{-5}	1 x 10^{-8}	7.7 x 10^{-7}	1 x 10^{-15}
400	1.0000	4.04 x 10^{-5}	3 x 10^{-8}	8.5 x 10^{-7}	2 x 10^{-15}
500	1.0000	4.04 x 10^{-5}	1 x 10^{-8}	7.9 x 10^{-7}	1 x 10^{-15}
600	1.0000	3.91 x 10^{-5}	0	8.2 x 10^{-7}	1 x 10^{-15}
700	1.0000	4.06 x 10^{-5}	0	8.3 x 10^{-7}	2 x 10^{-15}
760	1.0000	3.99 x 10^{-5}	2 x 10^{-8}	9.1 x 10^{-7}	2 x 10^{-15}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 6S: RRKM/ME Yields and Triplet Rate Coefficients at 240 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	7.39×10^{-5}	0.9998	5.9×10^{-6}	7.47×10^{-5}	2.1×10^{-13}
10	7.50×10^{-5}	0.9998	5.5×10^{-6}	7.43×10^{-5}	2.1×10^{-13}
20	7.48×10^{-5}	0.9998	5.7×10^{-6}	7.54×10^{-5}	2.1×10^{-13}
30	7.66×10^{-5}	0.9998	5.7×10^{-6}	7.50×10^{-5}	2.1×10^{-13}
40	7.54×10^{-5}	0.9998	6.2×10^{-6}	7.30×10^{-5}	2.1×10^{-13}
50	7.50×10^{-5}	0.9998	6.2×10^{-6}	7.26×10^{-5}	2.1×10^{-13}
100	7.42×10^{-5}	0.9998	5.8×10^{-6}	7.44×10^{-5}	2.1×10^{-13}
200	7.41×10^{-5}	0.9998	5.8×10^{-6}	7.43×10^{-5}	2.1×10^{-13}
300	7.62×10^{-5}	0.9998	5.9×10^{-6}	7.30×10^{-5}	2.1×10^{-13}
400	7.45×10^{-5}	0.9998	5.7×10^{-6}	7.47×10^{-5}	2.1×10^{-13}
500	7.54×10^{-5}	0.9998	6.1×10^{-6}	7.44×10^{-5}	2.1×10^{-13}
600	7.64×10^{-5}	0.9998	5.8×10^{-6}	7.53×10^{-5}	2.1×10^{-13}
700	7.46×10^{-5}	0.9998	5.8×10^{-6}	7.39×10^{-5}	2.1×10^{-13}
760	7.50×10^{-5}	0.9998	6.0×10^{-6}	7.35×10^{-5}	2.1×10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 7S: RRKM/ME Yields and Triplet Rate Coefficients at 250 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9876	1.020×10^{-4}	0.01234	1.6×10^{-7}	2.25×10^{-11}
10	0.9875	1.018×10^{-4}	0.01236	1.8×10^{-7}	2.27×10^{-11}
20	0.9875	1.009×10^{-4}	0.01238	1.4×10^{-7}	2.27×10^{-11}
30	0.9875	1.009×10^{-4}	0.01238	2.1×10^{-7}	2.27×10^{-11}
40	0.9875	1.030×10^{-4}	0.01239	2.3×10^{-7}	2.27×10^{-11}
50	0.9875	9.948×10^{-5}	0.01240	1.8×10^{-7}	2.27×10^{-11}
100	0.9874	1.030×10^{-4}	0.01247	1.2×10^{-7}	2.29×10^{-11}
200	0.9873	1.006×10^{-4}	0.01259	2.2×10^{-7}	2.30×10^{-11}
300	0.9872	9.976×10^{-5}	0.01271	1.8×10^{-7}	2.32×10^{-11}
400	0.9871	1.011×10^{-4}	0.01281	1.7×10^{-7}	2.34×10^{-11}
500	0.9870	1.003×10^{-4}	0.01294	1.8×10^{-7}	2.36×10^{-11}
600	0.9868	1.004×10^{-4}	0.01307	2.0×10^{-7}	2.40×10^{-11}
700	0.9867	1.011×10^{-4}	0.01317	6.0×10^{-8}	2.41×10^{-11}
760	0.9867	1.013×10^{-4}	0.01324	1.2×10^{-7}	2.41×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 8S: RRKM/ME Yields and Triplet Rate Coefficients at 250 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	4.19 x 10^{-5}	0	1.3 x 10^{-6}	2 x 10^{-15}
10	1.0000	4.17 x 10^{-5}	1 x 10^{-8}	8.4 x 10^{-7}	2 x 10^{-15}
20	1.0000	4.28 x 10^{-5}	1 x 10^{-8}	1.1 x 10^{-6}	2 x 10^{-15}
30	1.0000	4.28 x 10^{-5}	2 x 10^{-8}	1.1 x 10^{-6}	2 x 10^{-15}
40	1.0000	4.25 x 10^{-5}	1 x 10^{-8}	1.0 x 10^{-6}	2 x 10^{-15}
50	1.0000	4.15 x 10^{-5}	0	1.0 x 10^{-6}	2 x 10^{-15}
100	1.0000	4.24 x 10^{-5}	2 x 10^{-8}	8.9 x 10^{-7}	2 x 10^{-15}
200	1.0000	4.14 x 10^{-5}	2 x 10^{-8}	9.3 x 10^{-7}	2 x 10^{-15}
300	1.0000	4.21 x 10^{-5}	1 x 10^{-8}	1.1 x 10^{-6}	2 x 10^{-15}
400	1.0000	4.20 x 10^{-5}	1 x 10^{-8}	1.0 x 10^{-6}	2 x 10^{-15}
500	1.0000	4.21 x 10^{-5}	0	9.3 x 10^{-7}	2 x 10^{-15}
600	1.0000	4.13 x 10^{-5}	3 x 10^{-8}	8.0 x 10^{-7}	2 x 10^{-15}
700	1.0000	4.13 x 10^{-5}	2 x 10^{-8}	8.4 x 10^{-7}	2 x 10^{-15}
760	1.0000	4.27 x 10^{-5}	0	9.3 x 10^{-7}	2 x 10^{-15}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 9S: RRKM/ME Yields and Triplet Rate Coefficients at 250 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	8.00×10^{-5}	0.9998	5.1×10^{-6}	7.50×10^{-5}	2.0×10^{-13}
10	7.94×10^{-5}	0.9998	5.0×10^{-6}	7.60×10^{-5}	2.0×10^{-13}
20	8.14×10^{-5}	0.9998	5.2×10^{-6}	7.44×10^{-5}	2.0×10^{-13}
30	8.02×10^{-5}	0.9998	5.7×10^{-6}	7.42×10^{-5}	2.0×10^{-13}
40	7.80×10^{-5}	0.9998	5.9×10^{-6}	7.74×10^{-5}	2.1×10^{-13}
50	7.96×10^{-5}	0.9998	5.2×10^{-6}	7.54×10^{-5}	2.0×10^{-13}
100	8.08×10^{-5}	0.9998	5.5×10^{-6}	7.51×10^{-5}	2.0×10^{-13}
200	7.88×10^{-5}	0.9998	5.3×10^{-6}	7.50×10^{-5}	2.0×10^{-13}
300	8.02×10^{-5}	0.9998	5.5×10^{-6}	7.48×10^{-5}	2.0×10^{-13}
400	8.08×10^{-5}	0.9998	5.6×10^{-6}	7.56×10^{-5}	2.0×10^{-13}
500	8.07×10^{-5}	0.9998	5.3×10^{-6}	7.52×10^{-5}	2.0×10^{-13}
600	7.85×10^{-5}	0.9998	5.4×10^{-6}	7.54×10^{-5}	2.0×10^{-13}
700	7.97×10^{-5}	0.9998	5.6×10^{-6}	7.60×10^{-5}	2.0×10^{-13}
760	7.97×10^{-5}	0.9998	5.6×10^{-6}	7.52×10^{-5}	2.0×10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 10S: RRKM/ME Yields and Triplet Rate Coefficients at 260 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9891	9.95×10^{-5}	0.01085	1.6×10^{-7}	1.98×10^{-11}
10	0.9890	1.01×10^{-4}	0.01087	1.6×10^{-7}	2.00×10^{-11}
20	0.9890	9.90×10^{-5}	0.01087	1.8×10^{-7}	2.00×10^{-11}
30	0.9890	9.78×10^{-5}	0.01089	2.0×10^{-7}	2.00×10^{-11}
40	0.9890	1.01×10^{-4}	0.01088	2.7×10^{-7}	2.00×10^{-11}
50	0.9890	9.75×10^{-5}	0.01089	1.2×10^{-7}	2.00×10^{-11}
100	0.9889	1.01×10^{-4}	0.01096	1.2×10^{-7}	2.01×10^{-11}
200	0.9888	9.84×10^{-5}	0.01105	2.1×10^{-7}	2.03×10^{-11}
300	0.9888	9.72×10^{-5}	0.01112	1.5×10^{-7}	2.03×10^{-11}
400	0.9887	9.83×10^{-5}	0.01123	1.8×10^{-7}	2.05×10^{-11}
500	0.9886	9.89×10^{-5}	0.01133	1.3×10^{-7}	2.07×10^{-11}
600	0.9885	9.86×10^{-5}	0.01142	1.9×10^{-7}	2.09×10^{-11}
700	0.9884	9.96×10^{-5}	0.01151	1.6×10^{-7}	2.11×10^{-11}
760	0.9883	9.87×10^{-5}	0.01155	1.9×10^{-7}	2.12×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 11S: RRKM/ME Yields and Triplet Rate Coefficients at 260 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	4.34×10^{-5}	2×10^{-8}	1.2×10^{-6}	2×10^{-15}
10	1.0000	4.32×10^{-5}	0	1.1×10^{-6}	2×10^{-15}
20	1.0000	4.36×10^{-5}	2×10^{-8}	1.2×10^{-6}	2×10^{-15}
30	1.0000	4.44×10^{-5}	0	1.1×10^{-6}	2×10^{-15}
40	1.0000	4.32×10^{-5}	2×10^{-8}	1.3×10^{-6}	2×10^{-15}
50	1.0000	4.27×10^{-5}	1×10^{-8}	1.2×10^{-6}	2×10^{-15}
100	1.0000	4.36×10^{-5}	0	1.2×10^{-6}	2×10^{-15}
200	1.0000	4.29×10^{-5}	0	1.2×10^{-6}	2×10^{-15}
300	1.0000	4.42×10^{-5}	1×10^{-8}	1.1×10^{-6}	2×10^{-15}
400	1.0000	4.32×10^{-5}	2×10^{-8}	1.4×10^{-6}	3×10^{-15}
500	1.0000	4.37×10^{-5}	0	9.3×10^{-7}	2×10^{-15}
600	1.0000	4.25×10^{-5}	2×10^{-8}	1.1×10^{-6}	2×10^{-15}
700	1.0000	4.27×10^{-5}	3×10^{-8}	1.1×10^{-6}	2×10^{-15}
760	1.0000	4.40×10^{-5}	0	9.8×10^{-7}	2×10^{-15}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 12S: RRKM/ME Yields and Triplet Rate Coefficients at 260 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	8.57 x 10^{-5}	0.9998	5.0 x 10^{-6}	7.56 x 10^{-5}	1.9 x 10^{-13}
10	8.62 x 10^{-5}	0.9998	4.6 x 10^{-6}	7.74 x 10^{-5}	1.9 x 10^{-13}
20	8.42 x 10^{-5}	0.9998	5.1 x 10^{-6}	7.85 x 10^{-5}	2.0 x 10^{-13}
30	8.58 x 10^{-5}	0.9998	5.3 x 10^{-6}	7.69 x 10^{-5}	1.9 x 10^{-13}
40	8.52 x 10^{-5}	0.9998	5.1 x 10^{-6}	7.54 x 10^{-5}	1.9 x 10^{-13}
50	8.42 x 10^{-5}	0.9998	5.0 x 10^{-6}	7.72 x 10^{-5}	1.9 x 10^{-13}
100	8.33 x 10^{-5}	0.9998	5.2 x 10^{-6}	7.52 x 10^{-5}	2.0 x 10^{-13}
200	8.59 x 10^{-5}	0.9998	4.9 x 10^{-6}	7.57 x 10^{-5}	1.9 x 10^{-13}
300	8.57 x 10^{-5}	0.9998	5.2 x 10^{-6}	7.59 x 10^{-5}	1.9 x 10^{-13}
400	8.51 x 10^{-5}	0.9998	5.1 x 10^{-6}	7.66 x 10^{-5}	1.9 x 10^{-13}
500	8.61 x 10^{-5}	0.9998	5.3 x 10^{-6}	7.77 x 10^{-5}	1.9 x 10^{-13}
600	8.52 x 10^{-5}	0.9998	5.5 x 10^{-6}	7.60 x 10^{-5}	1.9 x 10^{-13}
700	8.47 x 10^{-5}	0.9998	5.0 x 10^{-6}	7.64 x 10^{-5}	1.9 x 10^{-13}
760	8.67 x 10^{-5}	0.9998	5.3 x 10^{-6}	7.87 x 10^{-5}	1.9 x 10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 13S: RRKM/ME Yields and Triplet Rate Coefficients at 270 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9903	9.81×10^{-5}	0.00958	1.1×10^{-7}	1.76×10^{-11}
10	0.9903	9.84×10^{-5}	0.00959	2.0×10^{-7}	1.76×10^{-11}
20	0.9903	9.88×10^{-5}	0.00959	1.6×10^{-7}	1.76×10^{-11}
30	0.9903	9.59×10^{-5}	0.00961	2.5×10^{-7}	1.76×10^{-11}
40	0.9903	9.80×10^{-5}	0.00961	2.3×10^{-7}	1.76×10^{-11}
50	0.9903	9.61×10^{-5}	0.00962	2.4×10^{-7}	1.76×10^{-11}
100	0.9902	9.86×10^{-5}	0.00966	1.4×10^{-7}	1.78×10^{-11}
200	0.9902	9.61×10^{-5}	0.00974	2.5×10^{-7}	1.78×10^{-11}
300	0.9901	9.51×10^{-5}	0.00981	1.3×10^{-7}	1.80×10^{-11}
400	0.9900	9.63×10^{-5}	0.00988	2.4×10^{-7}	1.82×10^{-11}
500	0.9899	9.82×10^{-5}	0.00996	2.2×10^{-7}	1.83×10^{-11}
600	0.9899	9.64×10^{-5}	0.01004	1.8×10^{-7}	1.83×10^{-11}
700	0.9898	9.75×10^{-5}	0.01011	2.0×10^{-7}	1.85×10^{-11}
760	0.9898	9.70×10^{-5}	0.01015	1.5×10^{-7}	1.85×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 14S: RRKM/ME Yields and Triplet Rate Coefficients at 270 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	4.51×10^{-5}	2×10^{-8}	1.4×10^{-6}	3×10^{-15}
10	1.0000	4.56×10^{-5}	1×10^{-8}	1.1×10^{-6}	2×10^{-15}
20	1.0000	4.59×10^{-5}	2×10^{-8}	1.4×10^{-6}	3×10^{-15}
30	1.0000	4.59×10^{-5}	0	1.3×10^{-6}	2×10^{-15}
40	1.0000	4.58×10^{-5}	2×10^{-8}	1.5×10^{-6}	3×10^{-15}
50	1.0000	4.45×10^{-5}	1×10^{-8}	1.2×10^{-6}	2×10^{-15}
100	1.0000	4.53×10^{-5}	1×10^{-8}	1.3×10^{-6}	2×10^{-15}
200	1.0000	4.67×10^{-5}	1×10^{-8}	1.3×10^{-6}	2×10^{-15}
300	1.0000	4.56×10^{-5}	2×10^{-8}	1.2×10^{-6}	2×10^{-15}
400	1.0000	4.45×10^{-5}	3×10^{-8}	1.3×10^{-6}	2×10^{-15}
500	1.0000	4.57×10^{-5}	7×10^{-8}	1.1×10^{-6}	2×10^{-15}
600	1.0000	4.65×10^{-5}	0	1.3×10^{-6}	2×10^{-15}
700	1.0000	4.42×10^{-5}	4×10^{-8}	1.2×10^{-6}	2×10^{-15}
760	1.0000	4.59×10^{-5}	1×10^{-8}	1.1×10^{-6}	2×10^{-15}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 15S: RRKM/ME Yields and Triplet Rate Coefficients at 270 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	9.08×10^{-5}	0.9998	4.7×10^{-6}	7.68×10^{-5}	1.8×10^{-13}
10	8.94×10^{-5}	0.9998	4.9×10^{-6}	7.82×10^{-5}	1.9×10^{-13}
20	9.04×10^{-5}	0.9998	4.8×10^{-6}	7.89×10^{-5}	1.8×10^{-13}
30	9.12×10^{-5}	0.9998	4.6×10^{-6}	7.76×10^{-5}	1.8×10^{-13}
40	9.12×10^{-5}	0.9998	4.8×10^{-6}	7.63×10^{-5}	1.8×10^{-13}
50	9.15×10^{-5}	0.9998	4.5×10^{-6}	7.77×10^{-5}	1.8×10^{-13}
100	9.05×10^{-5}	0.9998	4.5×10^{-6}	7.61×10^{-5}	1.8×10^{-13}
200	9.02×10^{-5}	0.9998	4.6×10^{-6}	7.70×10^{-5}	1.9×10^{-13}
300	8.99×10^{-5}	0.9998	5.0×10^{-6}	7.73×10^{-5}	1.9×10^{-13}
400	9.12×10^{-5}	0.9998	4.7×10^{-6}	7.77×10^{-5}	1.8×10^{-13}
500	9.07×10^{-5}	0.9998	5.0×10^{-6}	7.77×10^{-5}	1.8×10^{-13}
600	9.03×10^{-5}	0.9998	5.0×10^{-6}	7.73×10^{-5}	1.9×10^{-13}
700	9.12×10^{-5}	0.9998	4.7×10^{-6}	7.73×10^{-5}	1.8×10^{-13}
760	9.03×10^{-5}	0.9998	5.1×10^{-6}	7.77×10^{-5}	1.8×10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 16S: RRKM/ME Yields and Triplet Rate Coefficients at 280 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9914	9.59×10^{-5}	0.008500	1.5×10^{-7}	1.56×10^{-11}
10	0.9914	9.57×10^{-5}	0.008503	1.9×10^{-7}	1.56×10^{-11}
20	0.9914	9.65×10^{-5}	0.008507	2.3×10^{-7}	1.56×10^{-11}
30	0.9914	9.50×10^{-5}	0.008514	3.1×10^{-7}	1.56×10^{-11}
40	0.9914	9.71×10^{-5}	0.008521	2.4×10^{-7}	1.56×10^{-11}
50	0.9914	9.43×10^{-5}	0.008539	2.9×10^{-7}	1.56×10^{-11}
100	0.9913	9.72×10^{-5}	0.008567	1.4×10^{-7}	1.58×10^{-11}
200	0.9913	9.53×10^{-5}	0.008622	2.3×10^{-7}	1.58×10^{-11}
300	0.9912	9.41×10^{-5}	0.008687	1.9×10^{-7}	1.60×10^{-11}
400	0.9912	9.53×10^{-5}	0.008726	2.4×10^{-7}	1.60×10^{-11}
500	0.9911	9.64×10^{-5}	0.008794	3.1×10^{-7}	1.61×10^{-11}
600	0.9910	9.60×10^{-5}	0.008864	2.2×10^{-7}	1.63×10^{-11}
700	0.9910	9.50×10^{-5}	0.008914	2.7×10^{-7}	1.63×10^{-11}
760	0.9910	9.60×10^{-5}	0.008946	2.7×10^{-7}	1.63×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 17S: RRKM/ME Yields and Triplet Rate Coefficients at 280 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	4.71 x 10^{-5}	1 x 10^{-8}	1.5 x 10^{-6}	3 x 10^{-15}
10	1.0000	4.63 x 10^{-5}	2 x 10^{-8}	1.4 x 10^{-6}	3 x 10^{-15}
20	0.9999	4.85 x 10^{-5}	3 x 10^{-8}	1.5 x 10^{-6}	3 x 10^{-15}
30	1.0000	4.72 x 10^{-5}	0	1.5 x 10^{-6}	3 x 10^{-15}
40	1.0000	4.79 x 10^{-5}	3 x 10^{-8}	1.5 x 10^{-6}	3 x 10^{-15}
50	1.0000	4.62 x 10^{-5}	0	1.5 x 10^{-6}	3 x 10^{-15}
100	1.0000	4.72 x 10^{-5}	0	1.6 x 10^{-6}	3 x 10^{-15}
200	0.9999	4.87 x 10^{-5}	3 x 10^{-8}	1.4 x 10^{-6}	3 x 10^{-15}
300	1.0000	4.64 x 10^{-5}	2 x 10^{-8}	1.4 x 10^{-6}	3 x 10^{-15}
400	1.0000	4.67 x 10^{-5}	2 x 10^{-8}	1.5 x 10^{-6}	3 x 10^{-15}
500	1.0000	4.72 x 10^{-5}	6 x 10^{-8}	1.5 x 10^{-6}	3 x 10^{-15}
600	1.0000	4.83 x 10^{-5}	4 x 10^{-8}	1.3 x 10^{-6}	2 x 10^{-15}
700	1.0000	4.61 x 10^{-5}	5 x 10^{-8}	1.3 x 10^{-6}	3 x 10^{-15}
760	1.0000	4.77 x 10^{-5}	2 x 10^{-8}	1.2 x 10^{-6}	2 x 10^{-15}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 18S: RRKM/ME Yields and Triplet Rate Coefficients at 280 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	9.45×10^{-5}	0.9998	4.2×10^{-6}	7.97×10^{-5}	1.8×10^{-13}
10	9.68×10^{-5}	0.9998	4.3×10^{-6}	7.91×10^{-5}	1.7×10^{-13}
20	9.62×10^{-5}	0.9998	4.5×10^{-6}	8.07×10^{-5}	1.8×10^{-13}
30	9.69×10^{-5}	0.9998	4.5×10^{-6}	7.98×10^{-5}	1.7×10^{-13}
40	9.58×10^{-5}	0.9998	4.3×10^{-6}	8.00×10^{-5}	1.8×10^{-13}
50	9.74×10^{-5}	0.9998	4.6×10^{-6}	7.95×10^{-5}	1.7×10^{-13}
100	9.63×10^{-5}	0.9998	4.4×10^{-6}	7.77×10^{-5}	1.7×10^{-13}
200	9.61×10^{-5}	0.9998	4.3×10^{-6}	7.92×10^{-5}	1.8×10^{-13}
300	9.56×10^{-5}	0.9998	4.3×10^{-6}	7.78×10^{-5}	1.8×10^{-13}
400	9.63×10^{-5}	0.9998	4.4×10^{-6}	7.85×10^{-5}	1.8×10^{-13}
500	9.54×10^{-5}	0.9998	4.6×10^{-6}	7.95×10^{-5}	1.8×10^{-13}
600	9.61×10^{-5}	0.9998	4.5×10^{-6}	8.01×10^{-5}	1.8×10^{-13}
700	9.63×10^{-5}	0.9998	4.3×10^{-6}	7.81×10^{-5}	1.8×10^{-13}
760	9.39×10^{-5}	0.9998	4.6×10^{-6}	7.89×10^{-5}	1.8×10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 19S: RRKM/ME Yields and Triplet Rate Coefficients at 290 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3a[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	0.9923	9.50×10^{-5}	0.007571	2.1×10^{-7}	1.40×10^{-11}
10	0.9923	9.49×10^{-5}	0.007568	2.0×10^{-7}	1.40×10^{-11}
20	0.9923	9.55×10^{-5}	0.007571	2.0×10^{-7}	1.40×10^{-11}
30	0.9923	9.40×10^{-5}	0.007585	2.8×10^{-7}	1.40×10^{-11}
40	0.9923	9.58×10^{-5}	0.007592	3.7×10^{-7}	1.40×10^{-11}
50	0.9923	9.39×10^{-5}	0.007601	2.9×10^{-7}	1.40×10^{-11}
100	0.9923	9.52×10^{-5}	0.007625	1.8×10^{-7}	1.40×10^{-11}
200	0.9922	9.46×10^{-5}	0.007671	2.3×10^{-7}	1.41×10^{-11}
300	0.9922	9.34×10^{-5}	0.007725	3.1×10^{-7}	1.41×10^{-11}
400	0.9921	9.38×10^{-5}	0.007763	3.0×10^{-7}	1.43×10^{-11}
500	0.9921	9.46×10^{-5}	0.007799	3.1×10^{-7}	1.43×10^{-11}
600	0.9920	9.45×10^{-5}	0.007875	2.9×10^{-7}	1.45×10^{-11}
700	0.9920	9.49×10^{-5}	0.007893	2.8×10^{-7}	1.45×10^{-11}
760	0.9920	9.55×10^{-5}	0.007935	3.0×10^{-7}	1.45×10^{-11}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 20S: RRKM/ME Yields and Triplet Rate Coefficients at 290 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3f[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.0000	4.34×10^{-5}	2×10^{-8}	1.2×10^{-6}	2×10^{-15}
10	1.0000	4.32×10^{-5}	0	1.1×10^{-6}	2×10^{-15}
20	1.0000	4.36×10^{-5}	2×10^{-8}	1.2×10^{-6}	2×10^{-15}
30	1.0000	4.44×10^{-5}	0	1.1×10^{-6}	2×10^{-15}
40	1.0000	4.32×10^{-5}	2×10^{-8}	1.3×10^{-6}	2×10^{-15}
50	1.0000	4.27×10^{-5}	1×10^{-8}	1.2×10^{-6}	2×10^{-15}
100	1.0000	4.36×10^{-5}	0	1.2×10^{-6}	2×10^{-15}
200	1.0000	4.29×10^{-5}	0	1.2×10^{-6}	2×10^{-15}
300	1.0000	4.42×10^{-5}	1×10^{-8}	1.1×10^{-6}	2×10^{-15}
400	1.0000	4.32×10^{-5}	2×10^{-8}	1.4×10^{-6}	3×10^{-15}
500	1.0000	4.37×10^{-5}	0	9.3×10^{-7}	2×10^{-15}
600	1.0000	4.25×10^{-5}	2×10^{-8}	1.1×10^{-6}	2×10^{-15}
700	1.0000	4.27×10^{-5}	3×10^{-8}	1.1×10^{-6}	2×10^{-15}
760	1.0000	4.40×10^{-5}	0	9.8×10^{-7}	2×10^{-15}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 21S: RRKM/ME Yields and Triplet Rate Coefficients at 290 K for the Triplet Reaction Pathway Initiated by Formation of Complex 3h[a]

pressure (Torr)	**1-*syn* + 2**	**1-*anti* + 2**	**6-*syn* + 7**	**6-*anti* + 7**	k_{trip}[b]
1	1.01×10^{-4}	0.9998	4.2×10^{-6}	7.96×10^{-5}	1.7×10^{-13}
10	1.01×10^{-4}	0.9998	4.0×10^{-6}	7.94×10^{-5}	1.7×10^{-13}
20	9.95×10^{-5}	0.9998	3.8×10^{-6}	8.09×10^{-5}	1.7×10^{-13}
30	1.02×10^{-4}	0.9998	4.5×10^{-6}	8.00×10^{-5}	1.7×10^{-13}
40	1.02×10^{-4}	0.9998	4.5×10^{-6}	8.16×10^{-5}	1.7×10^{-13}
50	1.03×10^{-4}	0.9998	4.5×10^{-6}	8.02×10^{-5}	1.6×10^{-13}
100	1.03×10^{-4}	0.9998	4.2×10^{-6}	8.02×10^{-5}	1.6×10^{-13}
200	1.02×10^{-4}	0.9998	4.0×10^{-6}	8.10×10^{-5}	1.7×10^{-13}
300	1.01×10^{-4}	0.9998	4.0×10^{-6}	7.83×10^{-5}	1.7×10^{-13}
400	1.02×10^{-4}	0.9998	4.5×10^{-6}	7.97×10^{-5}	1.7×10^{-13}
500	9.95×10^{-5}	0.9998	4.2×10^{-6}	7.91×10^{-5}	1.7×10^{-13}
600	1.01×10^{-4}	0.9998	4.1×10^{-6}	7.95×10^{-5}	1.7×10^{-13}
700	1.03×10^{-4}	0.9998	4.4×10^{-6}	7.91×10^{-5}	1.6×10^{-13}
760	1.02×10^{-4}	0.9998	4.0×10^{-6}	8.05×10^{-5}	1.7×10^{-13}

[a]Simulations are of the mechanism in Figures 3 and 4. [b]In units of cm^3 $molecule^{-1}$ s^{-1}.

TABLE 22S: Individual Channel and Net Triplet Rate Coefficients at a Range of Tropospheric Temperatures with only Intermolecular Degrees of Freedom Active for $CH_3C(O)OO\text{-}HO_2$ Complexes and their Interconversion Transition Structures

T (K)	*syn:anti*[a]	k(**3a**)[b]	k(**3f**)[b]	k(**3h**)[b]	k_{1a}[b]	% change[c]
230	0.286:0.714	3.95×10^{-11}	8.39×10^{-14}	2.10×10^{-13}	1.15×10^{-11}	22
240	0.301:0.699	3.38×10^{-11}	8.65×10^{-14}	2.05×10^{-13}	1.03×10^{-11}	21
250	0.316:0.684	2.92×10^{-11}	8.48×10^{-14}	1.88×10^{-13}	9.37×10^{-12}	21
260	0.329:0.671	2.52×10^{-11}	8.48×10^{-14}	1.88×10^{-13}	8.44×10^{-12}	18
270	0.342:0.658	2.19×10^{-11}	8.37×10^{-14}	1.86×10^{-13}	7.63×10^{-12}	18
280	0.355:0.645	1.91×10^{-11}	8.49×10^{-14}	1.80×10^{-13}	6.92×10^{-12}	17
290	0.366:0.634	1.69×10^{-11}	8.38×10^{-14}	1.75×10^{-13}	6.33×10^{-12}	17
298.15	0.375:0.625	1.53×10^{-11}	8.31×10^{-14}	1.71×10^{-13}	5.86×10^{-12}	15

[a]Relative abundances of the *syn* and *anti* conformers of acetylperoxy based on W1BD zero-point-corrected electronic energies and B3LYP/cc-pVTZ+d partition functions. [b]In units of cm^3 $molecule^{-1}$ s^{-1}. [c]Compared to the values of k_{1a} obtained by assuming that all vibrational degrees of freedom were active and contributed to complex isomerization, as listed in Table 4.

Calculation of Capture Rate Constants

To calculate acetylperoxy-HO_2 capture rate constants, we used the long-range transition state theory results of Georgievskii and Klippenstein.[2] Specifically, we assumed that

$$k_{\text{cap}} = k_{\text{dipole-dipole}} + k_{\text{dipole-quadrupole}} + k_{\text{dipole-induced dipole}} + k_{\text{dispersion}} \tag{1S}$$

where the individual contributions to the overall capture rate constants are, in atomic units (au),

$$k_{\text{dipole-dipole}} = 5.87\mu^{-1/2}(d_{\text{acetylperoxy}}d_{\text{HO2}})^{2/3}T^{-1/6} \tag{2S}$$

$$k_{\text{dipole-quadrupole}} = 4.74\mu^{-1/2}(d_{\text{acetylperoxy}}Q_{\text{HO2}})^{1/2} + 4.74\mu^{-1/2}(d_{\text{HO2}}Q_{\text{acetylperoxy}})^{1/2} \tag{3S}$$

$$k_{\text{dipole-induced dipole}} = 9.76\mu^{-1/2}(d^2_{\text{acetylperoxy}}\alpha_{\text{HO2}})^{1/3}T^{1/6} + 9.76\mu^{-1/2}(d^2_{\text{HO2}}\alpha_{\text{acetylperoxy}})^{1/3}T^{1/6} \tag{4S}$$

$$k_{\text{dispersion}} = 8.55\mu^{-1/2}\left(\frac{1.5\alpha_{\text{acetylperoxy}}\alpha_{\text{HO2}}E_{\text{acetylperoxy}}E_{\text{HO2}}}{E_{\text{acetylperoxy}} + E_{\text{HO2}}}\right)^{1/3}T^{1/6} \tag{5S}$$

In the above equations, μ is the reduced mass, d_i is the dipole moment of species *i*, *T* is the absolute temperature, Q_i is the quadrupole moment of species *i*, α_i is the polarizability of species *i*, and E_i is the vertical ionization energy of species *i*. We evaluated the above equations with the parameters in Table 23S determined from quantum chemical calculations. Note that the dipole moment, quadrupole moment, polarizability, and vertical ionization energy are all different for the *syn* and *anti* conformers of acetylperoxy, leading to different values of k_{cap} for these two conformers.

TABLE 23S: Parameters for Capture Rate Constant Calculations

Parameter	Value (au)
μ	4.117 x 10^4
$d_{\text{acetylperoxy}}$, *syn* conformer	1.373[a]
$d_{\text{acetylperoxy}}$, *anti* conformer	1.110[a]
d_{HO2}	0.8695[a]
$Q_{\text{acetylperoxy}}$, *syn* conformer	1.511[a]
$Q_{\text{acetylperoxy}}$, *anti* conformer	2.103 [a]
Q_{HO2}	0.3037[a]
$\alpha_{\text{acetylperoxy}}$, *syn* conformer	35.91 [a]
$\alpha_{\text{acetylperoxy}}$, *anti* conformer	36.06 [a]
α_{HO2}	11.40 [a]
$E_{\text{acetylperoxy}}$, *syn* conformer	0.4017[b]
$E_{\text{acetylperoxy}}$, *anti* conformer	0.4018[b]
E_{HO2}	0.4282[b]

[a]Calculated from a natural bond order analysis of the CCSD/MG3 density computed with the B3LYP/cc-pVTZ+d optimized geometry. [b]Calculated from W1BD calculations on the neutral and +1 cation for a given species frozen at its B3LYP/cc-pVTZ+d optimized geometry.

Evaluating equations 1S-5S above with the parameters in Table 23S leads to k_{cap} values of 1.84 x 10^{-9} cm^3 $molecule^{-1}$ s^{-1} for *syn* acetylperoxy-HO_2 complexes and 1.69 x 10^{-9} cm^3 $molecule^{-1}$ s^{-1} for *anti* acetylperoxy-HO_2 complexes.

Optimized Geometries of the Stationary Points in This Paper

All geometries optimized with the B3LYP/cc-pVTZ+d model chemistry unless otherwise noted.

1-anti

C -0.55450200 -0.13099600 -0.00008700
O -1.47588000 -0.87613200 0.00003600
O 0.74407400 -0.76758200 -0.00000700
O 1.76364500 0.07403400 0.00001900
C -0.54969800 1.36104100 0.00000800
H -0.02395200 1.74019900 0.87461700
H -0.02400300 1.74029900 -0.87458700
H -1.58155400 1.69667600 0.00006000

1-*syn*

C -0.41245300 0.22817800 0.00077400
O -0.23522800 1.39552300 -0.00012900
O 0.68403100 -0.72176500 0.00026000
O 1.87407000 -0.14913100 -0.00031500
C -1.68733400 -0.55158500 -0.00027300
H -1.72771800 -1.19615700 -0.87865300
H -1.72916800 -1.19596600 0.87817300
H -2.52737700 0.13554200 -0.00105100

2

O 0.05536300 0.71861600 0.00000000
O 0.05536300 -0.61040400 0.00000000
H -0.88580700 -0.86569500 0.00000000

3a

C 0.73728800 0.23751900 -0.00015100
O 0.13034200 -0.78729200 -0.00026700
O 2.16669100 0.25382700 0.00003400
O 2.71207700 -0.95222000 0.00010200
C 0.23753100 1.64006700 -0.00023100
H 0.61818900 2.16347300 0.87775800
H 0.61861600 2.16352900 -0.87800000
H -0.84889500 1.63181700 -0.00051100
H -1.67002000 -0.97508600 -0.00044900
O -2.65522000 -0.92240100 -0.00055900
O -2.92474000 0.37693000 0.00112700

3b

C 0.93155800 -0.22347200 0.28953800
O 0.26680500 -0.31020200 1.27240000
O 0.97926000 0.98168800 -0.48882600
O 0.13769800 1.90852900 -0.06696800
C 1.83382800 -1.23062600 -0.33378400
H 1.36657400 -1.58871900 -1.25253000
H 2.78883500 -0.77989200 -0.59960900
H 1.97513600 -2.06073400 0.35095300
H -1.53376600 -0.04174500 0.85282900
O -2.29400800 -0.24063800 0.25576900
O -1.73839100 -0.68991700 -0.85814600

3c

C -1.76900000 -0.04906800 -0.03337600
O -2.26765500 -1.08555800 -0.28264400
O -0.31874900 0.06680500 0.19778800
O 0.31217100 -1.07994200 0.07354400
C -2.34822900 1.31618600 0.11252500
H -2.12952300 1.70703700 1.10659300
H -1.88746200 1.99051600 -0.60992200
H -3.42070300 1.26889900 -0.04636900
H 2.13152800 -0.63258700 0.22920600
O 3.04946300 -0.27855700 0.25271400
O 2.97596200 0.88518100 -0.38570200

3d

C -1.89282700 -0.21969600 0.06278300
O -2.59257400 -1.15900200 0.21425400
O -0.48104600 -0.55203800 -0.14656100
O 0.29683400 0.49574100 -0.33478900
C -2.21868900 1.23356100 0.05589800
H -1.65695600 1.75306500 0.83105600
H -1.93901600 1.68271500 -0.89598600
H -3.28576700 1.33537100 0.22572600
H 2.07755800 -0.08765300 -0.52233100
O 3.03828100 -0.29196300 -0.48284100
O 3.42266600 0.16142700 0.70612000

3e

C -1.00388400 -0.47247500 -0.24053800
O -0.83832900 -1.43183900 -0.91129600
O -0.32547600 0.72602000 -0.73606200
O -0.55875300 1.82696900 -0.04060400
C -1.77824900 -0.29439000 1.01669500
H -1.10957000 0.02684000 1.81412800
H -2.53643300 0.47745000 0.89693000
H -2.23549400 -1.24696200 1.26454400
H 1.71484700 0.27785800 -0.77043000
O 2.45129800 -0.04867900 -0.21258800
O 1.87869100 -0.43922100 0.91778600

3f

C -1.33993000 0.41374800 -0.02072600
O -2.44332500 0.16280000 -0.33964400
O -0.35198700 -0.67486700 0.18569000
O -0.86299600 -1.88375600 0.04649900
C -0.65522500 1.70514600 0.25823200
H -0.53879500 1.81602700 1.33838100
H 0.34271400 1.71463100 -0.17943800
H -1.26379000 2.51953100 -0.12260200
H 1.60726700 -0.77832800 0.18195800
O 2.55841600 -0.55988300 0.08433800
O 2.57783300 0.70755300 -0.30730000

3g

C 0.54771100 0.54744700 -0.28987000
O -0.27067900 0.99572700 -1.03924700
O 1.08810900 -0.71100100 -0.68628100
O 2.01424300 -1.18901900 0.13007700
C 1.09577700 1.15442500 0.95291800
H 0.94828000 0.48050700 1.79422100
H 2.16844800 1.31738900 0.85243800
H 0.58216700 2.09524300 1.12204000
H -1.90753100 0.26495800 -0.72811700
O -2.52094000 -0.24545800 -0.14520600
O -1.76727000 -0.64641600 0.86329900

3h

C 0.70401100 -0.19554700 -0.00005300
O -0.12422000 -1.05800000 -0.00009000
O 2.04361000 -0.68387000 -0.00000900
O 2.96785000 0.26443500 0.00001200
C 0.51509300 1.27895200 -0.00008000
H 0.99480500 1.71774900 0.87423300
H 0.99493200 1.71773100 -0.87433300
H -0.55238400 1.48139200 -0.00016900
H -1.92671700 -0.84730800 -0.00017300
O -2.87756600 -0.58542000 -0.00022500
O -2.86283000 0.74160600 0.00046700

TS-3ab

C -0.66898600 0.41093100 0.32419400
O -0.09122300 -0.23669200 1.13910600
O -1.69843100 -0.15600800 -0.49427900
O -1.89315400 -1.44678400 -0.28024100
C -0.53490700 1.85466000 -0.01864700
H -0.29074000 1.95734100 -1.07515300
H -1.48421100 2.36291800 0.15583800
H 0.24732700 2.29809400 0.58820600
H 1.64593300 -0.65472600 0.77318100
O 2.45749500 -0.64862100 0.21295600
O 2.11344300 0.04345700 -0.86196100

TS-3ah

C -0.73147400 0.07269000 -0.24128300
O -0.03751900 -0.89145000 -0.29181700
O -2.15849100 -0.10455100 -0.46312300
O -2.70632700 -0.49224300 0.68376100
C -0.37943600 1.49477100 -0.01488600
H -0.75107700 2.09205200 -0.84939800
H -0.89678000 1.84327700 0.88098600
H 0.69684100 1.59967100 0.09221400
H 1.78479400 -0.93494700 -0.06299400
O 2.75100100 -0.78830800 0.06337800
O 2.88029500 0.52594900 0.19232800

TS-3bg

C -0.54252000 0.36521000 0.30210500
O 0.01193800 0.07178700 1.31334400
O -0.97771000 -0.70251200 -0.59568900
O -2.10537300 -1.20255000 -0.10201800
C -0.92973600 1.69999500 -0.21726800
H -0.55766500 1.81132300 -1.23524600
H -2.01923800 1.75723900 -0.25651100
H -0.53369400 2.48122400 0.42411600
H 1.70391000 -0.51455600 0.86737300
O 2.43496600 -0.50058300 0.20219100
O 1.91620600 0.09305100 -0.85642200

TS-3cd

C -1.76857800 -0.04948800 -0.03418000
O -2.26597800 -1.08620700 -0.28495300
O -0.31885700 0.06727700 0.20011800
O 0.31300800 -1.07916500 0.07768200
C -2.34919500 1.31514900 0.11175700
H -2.14032900 1.70120500 1.10986900
H -1.88154600 1.99302700 -0.60282300
H -3.42015300 1.26848200 -0.05728900
H 2.13185800 -0.63165500 0.23238000
O 3.05109600 -0.28047800 0.24651000
O 2.97283200 0.88794500 -0.38280800

TS-3cf

C 1.42581800 -0.17648200 -0.04997500
O 2.23581200 0.40468100 -0.67609200
O 0.25049100 0.51520600 0.50287000
O 0.17555200 1.78995000 0.16394300
C 1.31506200 -1.60982900 0.34009800
H 1.33267500 -1.69749600 1.42715500
H 0.35861500 -2.00435800 -0.00364100
H 2.14113000 -2.16493800 -0.09256900
H -1.88549000 0.73536300 0.22262800
O -2.69325500 0.23160600 -0.00423200
O -2.26762600 -0.96028100 -0.39827700

TS-3de

C -1.23188400 -0.28911400 -0.20872400
O -1.55071700 -1.12560200 -0.98030600
O -0.33915300 0.73008800 -0.76332600
O -0.02628500 1.70647900 0.07375800
C -1.58709700 -0.11517600 1.22592300
H -0.68305100 -0.14922000 1.83219100
H -2.05583400 0.85300900 1.39290700
H -2.26088300 -0.92006800 1.50186800
H 1.92091600 0.46636400 -0.63038100
O 2.56443500 -0.13979900 -0.21218700
O 1.85081200 -0.89921000 0.60708900

TS-3ef

C -1.07378900 -0.39508300 0.23112400
O -1.54020700 -0.47502800 1.30634900
C -1.10852100 -1.30445200 -0.94018900
H -1.53645100 -0.77654600 -1.79315400
H -0.08499800 -1.57984900 -1.19601900
H -1.69481500 -2.18750100 -0.70452000
O -0.25583700 0.82467400 -0.08856000
O -1.06502600 1.82106300 -0.41331500
O 2.53387000 0.41553600 0.11156300
O 2.16726700 -0.85778000 0.07062800
H 1.68959100 0.91339300 0.05475700

TS-3eg

C 0.88987600 -0.54007600 -0.24818300
O 0.46793600 -1.45423200 -0.87354600
C 1.79123300 -0.52108500 0.93440800
H 2.66915400 0.09292100 0.74167200
H 1.26782400 -0.08123700 1.78245300
H 2.07665700 -1.54469600 1.15483100
O 0.43758800 0.75524900 -0.72428300
O 0.89268500 1.79240900 -0.04205700
O -2.45758200 0.01652900 -0.20850100
O -1.88867600 -0.13759900 0.97872700
H -1.71589100 0.12112600 -0.83902200

TS-3gh

C -0.55874400 0.18198800 0.52777800
O 0.25039100 -0.11122400 1.35802500
O -1.41236600 -0.89105100 0.13476200
O -2.32876800 -0.55858100 -0.76141000
C -0.80721500 1.50511500 -0.10558700
H -0.71605600 1.42636800 -1.18677400
H -1.82040000 1.84193900 0.11208400
H -0.07919800 2.20790400 0.28596500
H 1.95418100 -0.30446800 0.74521800
O 2.63503300 -0.31553000 0.03112000
O 1.96286400 -0.03540900 -1.07370300

TS-4b

C -1.08054100 -0.01288800 0.28076700
O -0.76187800 0.01164800 1.41561700
O -0.50164800 0.92659700 -0.68796100
O 0.49264900 1.63869200 -0.19174600
C -2.05930300 -0.86682800 -0.44751800
H -2.73244600 -0.25101600 -1.04289800
H -1.51447600 -1.52015100 -1.12985400
H -2.61787800 -1.46187100 0.26802400
H 1.66858000 0.48534500 0.25588400
O 2.25132100 -0.32681600 0.19314900
O 1.52396600 -1.24687200 -0.39789100

TS-4d

C 1.81383200 -0.18166200 0.03329500
O 2.61264100 -1.04252500 0.19295600
O 0.49864200 -0.64553600 -0.33225200
O -0.39218700 0.33556100 -0.52533700
C 1.98068500 1.29594700 0.15103700
H 1.74211100 1.78299000 -0.79342300
H 1.29891900 1.69984000 0.89808600
H 3.01068300 1.49277400 0.43064900
H -1.70476000 0.00950700 0.20022200
O -2.60102600 -0.10793700 0.68095200
O -3.50732800 0.00158300 -0.24651000

5b

C -1.36198700 -0.30545400 -0.00001300
O -0.29894700 -0.87842800 -0.00007500
O -1.45119000 1.04194900 0.00003400
O -0.14951000 1.65270500 0.00000100
C -2.72210400 -0.93527600 0.00002400
H -3.51309000 -0.19058600 0.00006900
H -2.81173200 -1.57009700 -0.88065300
H -2.81166700 -1.57013400 0.88068100
O 2.83865100 0.28460000 -0.00004400
O 3.21298000 -0.86074600 0.00006900
H 0.42515600 0.85454900 -0.00005000

5d

C -1.60748900 0.39632400 -0.00422500
O -1.96702900 1.53749900 -0.03523500
O -0.36203100 0.15094900 -0.53709400
O -0.00827100 -1.25950200 -0.48188100
C -2.37891900 -0.76922700 0.53773800
H -2.53891500 -1.51708100 -0.23792000
H -1.82619100 -1.25596000 1.33982000
H -3.33030600 -0.39757200 0.90479300
H 0.92565800 -1.16789500 -0.24359000
O 2.94762100 -0.38656300 0.27754900
O 3.22573400 0.77960700 0.15613800

6b

C -0.41409200 0.16729100 -0.00054200
O -0.12651700 1.34037700 -0.00002600
O 0.52844000 -0.80047400 -0.00021900
O 1.85112500 -0.23638300 0.00028100
H 1.63165900 0.72268500 0.00092400
C -1.79239900 -0.42065400 0.00016900
H -1.76934500 -1.50690000 -0.00000900
H -2.32341000 -0.06203300 0.88118800
H -2.32434700 -0.06173900 -0.88015700

6d

C -0.59536000 -0.13176600 0.00314200
O -1.57428800 -0.81991400 0.01095500
O 0.60435600 -0.80702400 -0.02842900
O 1.74281000 0.10055800 -0.06066200
H 2.34602000 -0.39887700 0.50625800
C -0.55517700 1.36674200 0.01069900
H -0.01043900 1.73181000 0.88005500
H -0.03659000 1.74106800 -0.87106800
H -1.57878900 1.72719000 0.02680300

7

O 0.00000000 0.00000000 0.60290900
O 0.00000000 0.00000000 -0.60290900

8a

C -0.73723900 0.23760200 0.00001300
O -0.13025800 -0.78715200 0.00003700
C -0.23843100 1.64055900 0.00001600
H -0.62002900 2.16347700 -0.87783300
H -0.62000000 2.16345700 0.87788900
H 0.84798500 1.63343000 0.00000000
O -2.16682000 0.25346300 -0.00002500
O -2.71178500 -0.95277000 -0.00001500
O 2.65555300 -0.92228300 0.00000000
O 2.92527600 0.37693500 -0.00002900
H 1.67033300 -0.97487700 0.00002500

8b

C -0.93411700 -0.22503700 0.28993800
O -0.26516900 -0.30749400 1.26995200
O -0.98839900 0.97892900 -0.49110500
O -0.14996300 1.90983200 -0.07226100
C -1.83240800 -1.23790100 -0.32957400
H -1.34599800 -1.62152700 -1.22808000
H -1.99492300 -2.05164300 0.37010600
H -2.77722300 -0.78670300 -0.62804200
O 1.74982800 -0.69994700 -0.85118000
O 2.30094900 -0.22368300 0.25405100
H 1.53932400 -0.02360000 0.84817200

8b (ωB97X-D/cc-pVTZ+d)

C -0.91482300 -0.20388700 0.29497100
O -0.28329600 -0.25843200 1.29824400
O -0.94831300 0.96886000 -0.50642100
O -0.12218200 1.89423900 -0.09955000
C -1.78041500 -1.23916400 -0.32780200
H -1.26116900 -1.62640500 -1.20501500
H -1.94775100 -2.04241000 0.38172900
H -2.72302000 -0.80642800 -0.65667500
O 1.66726200 -0.72537800 -0.82375700
O 2.25837000 -0.23722000 0.23501700
H 1.52863500 -0.00299600 0.84867800

8c

C 1.77746100 -0.04918900 -0.02164600
O 2.28621000 -1.09806100 -0.18388100
C 2.35169000 1.32239700 0.07704400
H 1.92554800 1.95748300 -0.70006400
H 2.08838100 1.76502100 1.03808400
H 3.43026400 1.26744800 -0.02952900
O 0.31739900 0.07918300 0.12483300
O -0.30805700 -1.07445700 0.04349700
O -3.06287900 -0.33300000 0.16397300
O -2.99351700 0.92931700 -0.24644600
H -2.13233700 -0.65305600 0.14331600

8d

C 1.89714500 -0.22027200 0.06581300
O 2.59331500 -1.16114800 0.22312500
C 2.22545500 1.23239400 0.06369600
H 1.95575600 1.68303000 -0.89036000
H 1.65710400 1.75196000 0.83397500
H 3.29100100 1.33224400 0.24398900
O 0.48635300 -0.54985700 -0.15826500
O -0.28751000 0.49931300 -0.35304400
O -3.03749200 -0.30003400 -0.47207800
O -3.44971200 0.16726300 0.70227700
H -2.07909100 -0.08427300 -0.50078100

8e

C 1.00638200 -0.47209900 -0.23897600
O 0.84384100 -1.43429500 -0.90660900
C 1.77778700 -0.28873600 1.01931300
H 2.53461700 0.48442300 0.89938100
H 1.10632900 0.03326900 1.81411600
H 2.23647600 -1.23963100 1.27090500
O 0.32625100 0.72276300 -0.73930000
O 0.55493300 1.82619600 -0.04611300
O -2.45242800 -0.05575700 -0.21513800
O -1.88092100 -0.43115700 0.92087100
H -1.71584200 0.26494800 -0.77611900

8e (ωB97X-D/cc-pVTZ+d)

C 0.92748800 -0.48859000 -0.25051700
O 0.68591400 -1.43138700 -0.91846400
C 1.69859700 -0.38472500 1.01501600
H 2.52099800 0.31937500 0.90793100
H 1.04675900 -0.01460700 1.80411100
H 2.06833400 -1.37467500 1.25984600
O 0.37618700 0.74650500 -0.75384700
O 0.64768900 1.80375900 -0.03573400
O -2.39023700 -0.04620500 -0.19444600
O -1.78310900 -0.31050900 0.93455700
H -1.68414000 0.21249200 -0.81540600

8f

C 1.34035600 0.41354100 -0.02070800
O 2.44405800 0.16184700 -0.33804300
C 0.65580700 1.70539600 0.25677900
H -0.34138200 1.71527200 -0.18255300
H 0.53749100 1.81648600 1.33671400
H 1.26543800 2.51942600 -0.12309800
O 0.35160200 -0.67444700 0.18473600
O 0.86217500 -1.88362700 0.04667400
O -2.55835300 -0.56017400 0.08345800
O -2.57841500 0.70812100 -0.30523800
H -1.60705100 -0.77856300 0.17980900

8g

C 0.55099900 0.54301200 -0.29415600
O -0.26695000 0.97788500 -1.05108800
C 1.08293400 1.16044700 0.95039200
H 0.93837800 0.48742500 1.79287100
H 2.15409100 1.33676700 0.85633800
H 0.55642300 2.09521200 1.11337600
O 1.10886300 -0.71175300 -0.68154800
O 2.03197200 -1.17708900 0.14534700
O -2.53201700 -0.25211300 -0.15152200
O -1.78378600 -0.63612500 0.86829000
H -1.91713800 0.25340400 -0.73583200

8h

C 0.70392100 -0.19562600 0.00007300
O -0.12425000 -1.05809200 0.00011800
C 0.51545100 1.27894200 0.00015700
H 0.99588700 1.71724600 0.87433300
H 0.99569000 1.71732400 -0.87408800
H -0.55186600 1.48208000 0.00029800
O 2.04365400 -0.68390300 -0.00006000
O 2.96785200 0.26445600 -0.00008800
O -2.87775700 -0.58527000 0.00029700
O -2.86312400 0.74165000 -0.00053800
H -1.92693900 -0.84726700 0.00024600

TS-8ab

C -0.67242100 0.41301600 0.32408100
O -0.09020500 -0.22465800 1.14350300
C -0.55217500 1.85625400 -0.02560200
H -0.29561500 1.95520900 -1.07962200
H -1.50979300 2.35389400 0.13301800
H 0.21681300 2.31321100 0.58814500
O -1.69349400 -0.16857500 -0.49500400
O -1.87326400 -1.46090000 -0.27722800
O 2.45735200 -0.64304800 0.21362800
O 2.11060300 0.04820100 -0.86108500
H 1.64823700 -0.64610800 0.77706600

TS-8ah

C -0.73155900 0.07328600 -0.24170400
O -0.03667100 -0.89006700 -0.29327800
C -0.38110900 1.49554300 -0.01389300
H -0.75427100 2.09343100 -0.84727600
H -0.89814200 1.84214200 0.88289500
H 0.69511500 1.60160200 0.09241700
O -2.15866100 -0.10538100 -0.46310300
O -2.70528100 -0.49403800 0.68401200
O 2.75219400 -0.78848900 0.06482500
O 2.87926800 0.52628300 0.19113100
H 1.78651000 -0.93661300 -0.06314300

TS-8bc

C -1.30137400 -0.04673300 0.17583800
O -1.42126000 -0.57550600 1.22078800
C -1.97692900 1.14433000 -0.41055100
H -1.24326200 1.94365800 -0.52310800
H -2.36491300 0.91073300 -1.40155500
H -2.77839000 1.46391800 0.24787500
O -0.34274400 -0.54222300 -0.82626500
O 0.42408900 -1.51104400 -0.37060200
O 2.55369800 0.13142300 0.14921900
O 1.80084300 1.21096500 0.22205000
H 1.93937300 -0.61281300 -0.07645800

TS-8bg

C -0.54168200 0.36444600 0.30221400
O 0.01150100 0.06700500 1.31298900
C -0.92238200 1.70190300 -0.21515900
H -0.55239800 1.81210200 -1.23399800
H -2.01165400 1.76553800 -0.25137300
H -0.52016900 2.48020200 0.42595400
O -0.98251200 -0.69960000 -0.59704100
O -2.11036300 -1.19790600 -0.10206400
O 2.43690400 -0.50062600 0.20202600
O 1.91467100 0.08853600 -0.85731700
H 1.70699000 -0.51519900 0.86834300

TS-8cd

C -1.63646500 0.07399000 0.07597500
O -2.61330000 -0.55949500 -0.08474500
C -1.34016800 1.51764700 -0.09728700
H -1.04955700 1.93957700 0.86644800
H -0.48182800 1.63230400 -0.76007800
H -2.21277800 2.03161900 -0.48881700
O -0.41185400 -0.62494300 0.58572600
O 0.20671500 -1.17202000 -0.44511100
O 2.81971600 -0.35140600 0.04218900
O 2.45100100 0.92159000 -0.02360500
H 1.98573300 -0.86311600 -0.08530500

TS-8cf

C 1.44129600 -0.16780600 0.05032300
O 2.24809200 0.43181400 0.66305200
C 1.34919100 -1.60589700 -0.32704300
H 0.39367900 -2.00800600 0.01043300
H 1.37865400 -1.70243700 -1.41319800
H 2.17744000 -2.14823600 0.11749300
O 0.24929200 0.49895200 -0.49617500
O 0.15406200 1.77430400 -0.16550600
O -2.70678600 0.23225500 0.00216100
O -2.29449900 -0.96567600 0.39276000
H -1.89397700 0.72770500 -0.22474800

TS-8de

C 1.23897400 -0.28420100 -0.20931200
O 1.57004400 -1.10537000 -0.99220900
C 1.57450700 -0.13720000 1.23307400
H 2.03574200 0.82969400 1.42605700
H 0.66222400 -0.18818100 1.82577800
H 2.24852400 -0.94432000 1.50189300
O 0.34957500 0.74196200 -0.75590800
O 0.02561000 1.70299100 0.09444300
O -2.57290900 -0.14021600 -0.22208200
O -1.85932100 -0.90506200 0.59211600
H -1.93136700 0.47677000 -0.62717900

TS-8ef

C -1.07378800 -0.39508400 0.23112400
O -1.54020700 -0.47502700 1.30634900
C -1.10852100 -1.30445300 -0.94018900
H -1.53645000 -0.77654700 -1.79315300
H -0.08499700 -1.57985000 -1.19601900
H -1.69481500 -2.18750200 -0.70452000
O -0.25583700 0.82467400 -0.08856000
O -1.06502700 1.82106300 -0.41331500
O 2.53387100 0.41553600 0.11156300
O 2.16726700 -0.85778000 0.07062900
H 1.68959000 0.91339400 0.05475600

TS-8eg

C 0.88987600 -0.54007600 -0.24818300
O 0.46793600 -1.45423200 -0.87354600
C 1.79123300 -0.52108500 0.93440800
H 2.66915400 0.09292100 0.74167200
H 1.26782400 -0.08123700 1.78245300
H 2.07665700 -1.54469600 1.15483100
O 0.43758800 0.75524900 -0.72428300
O 0.89268500 1.79240900 -0.04205700
O -2.45758200 0.01652900 -0.20850100
O -1.88867600 -0.13759900 0.97872700
H -1.71589100 0.12112600 -0.83902200

TS-8gh

C -0.55710500 0.30600500 0.47326100
O 0.25233000 0.22497100 1.34944400
C -0.82122100 1.44231500 -0.45006800
H -0.72606100 1.11568500 -1.48337200
H -1.83931700 1.80692200 -0.31627600
H -0.10364100 2.22658500 -0.23265400
O -1.39533300 -0.84105100 0.33944200
O -2.31133400 -0.73857300 -0.61120400
O 2.63098600 -0.30288400 0.09572800
O 1.94571000 -0.28243000 -1.03616400
H 1.96009700 -0.11937300 0.79517600

TS-9b

C 1.10741100 -0.22430800 -0.06326700
O 0.43653100 -1.17398400 -0.36358900
O 0.62576500 1.06870000 0.02137200
O -0.61348300 1.23350600 -0.52287700
C 2.56210900 -0.23935400 0.29133300
H 2.78727000 0.50688800 1.04990500
H 2.83853200 -1.23275800 0.63169200
H 3.14173700 0.00367000 -0.60128500
O -1.87847200 0.24202700 0.67425900
O -2.24518200 -0.77823000 -0.08186500
H -1.38592100 -1.23198100 -0.26711200

TS-9b (ωB97X-D/cc-pVTZ IRCmax geometry)

C 1.18811300 -0.23691400 -0.06805100
O 0.50649500 -1.15976800 -0.38700200
O 0.72875100 1.08140200 -0.03488600
O -0.43433600 1.25401700 -0.62906200
C 2.62222100 -0.25960400 0.33535300
H 2.79110800 0.40059600 1.18330100
H 2.91674000 -1.27657800 0.57113700
H 3.22100800 0.11005200 -0.49805800
O -1.93262800 0.13174400 0.82526400
O -2.20604300 -0.81844500 -0.03041200
H -1.32517600 -1.08209900 -0.37464000

TS-9e (ωB97X-D/cc-pVTZ IRCmax geometry)

C 1.10741100 -0.22430800 -0.06326700
O 0.43653100 -1.17398400 -0.36358900
O 0.62576500 1.06870000 0.02137200
O -0.61348300 1.23350600 -0.52287700
C 2.56210900 -0.23935400 0.29133300
H 2.78727000 0.50688800 1.04990500
H 2.83853200 -1.23275800 0.63169200
H 3.14173700 0.00367000 -0.60128500
O -1.87847200 0.24202700 0.67425900
O -2.24518200 -0.77823000 -0.08186500
H -1.38592100 -1.23198100 -0.26711200

TS-9e (ωB97X-D/cc-pVTZ IRCmax geometry)

C -1.39567500 -0.20092300 -0.05914200
O -2.05324500 -1.14132500 -0.35274000
C -1.59952600 1.22774300 -0.43440600
H -1.66169600 1.85368600 0.45303100
H -0.75088200 1.58060700 -1.01809400
H -2.51482200 1.29019200 -1.01347300
O -0.26380700 -0.48376300 0.74715100
O 0.44958500 0.58254800 1.05829000
O 2.47612700 -0.54026900 -0.39485600
O 1.83011500 0.59208000 -0.54102300
H 1.88567900 -1.22703600 -0.74728800

10b

C -1.09980400 0.19816100 -0.03894900
O -0.55155800 1.25714600 -0.20855600
O -0.49499700 -1.01330900 -0.00555800
O 0.92763600 -1.03105800 -0.45348300
C -2.57768100 0.01420500 0.18029400
H -2.80392900 -0.93051700 0.66659100
H -2.94936000 0.84965100 0.76806100
H -3.06700000 0.03137700 -0.79476800
O 1.72725800 -0.40933200 0.48915000
O 2.09918500 0.87747300 -0.00483800
H 1.22501100 1.32793600 -0.02167100

10e

C 1.40162700 -0.22337500 -0.02508500
O 2.19327700 -1.08043800 -0.27372300
O 0.18500700 -0.67470400 0.48700900
O -0.75659500 0.40227000 0.76131200
C 1.59112600 1.25368000 -0.19164400
H 1.43548800 1.77322900 0.75256400
H 2.60219000 1.41830600 -0.55027300
H 0.87368700 1.65583800 -0.90602300
O -1.57150800 0.53762300 -0.36414900
O -2.62981500 -0.41429700 -0.27321100
H -2.23080900 -1.19284300 -0.69378900

10i

H 3.12187400 -0.48045100 -0.96611500
C 2.45280100 -0.83402300 -0.18656900
H 2.09224400 -1.83441600 -0.41458100
H 3.00141800 -0.87688700 0.75537200
C 1.32359000 0.15148300 -0.03916800
O 1.34126900 1.31393300 -0.29021800
O 0.22668000 -0.52927200 0.47570900
O -0.86527600 0.38681200 0.78948300
O -1.67074200 0.48668400 -0.32750100
O -2.62129500 -0.58881700 -0.29830600
H -2.15896600 -1.26772800 -0.81358500

10j

C 1.41342900 -0.20425900 -0.03646700
O 2.25139800 -1.00746400 -0.31087900
O 0.21826800 -0.73927400 0.44294600
O -0.75579200 0.27041700 0.80176800
C 1.52756000 1.28638800 -0.14768200
H 1.34915300 1.76248100 0.81523500
H 2.52855600 1.51457000 -0.49966600
H 0.79018700 1.67663900 -0.84808600
O -1.55243300 0.53947900 -0.32161700
O -2.54848300 -0.47336000 -0.43240600
H -3.21748900 -0.16485300 0.19892100

10k

C -1.17570900 0.17326500 -0.13180800
O -0.93141500 1.18492500 -0.71127100
O -0.31761800 -0.90871900 -0.02280900
O 0.92473000 -0.66917700 -0.74692200
C -2.45540700 -0.18926500 0.57503800
H -2.25686700 -0.70269200 1.51356500
H -3.02147700 0.72089600 0.74963100
H -3.03751300 -0.85886800 -0.05916500
O 1.93165700 -0.49916400 0.18524800
O 1.88421800 0.83899800 0.69656500
H 2.16997700 1.36175700 -0.06989600

10l

C 1.34968000 -0.05568300 -0.07900700
O 2.30338400 -0.46090400 -0.67142500
O 0.34505500 -0.99521500 0.12190900
O -0.81137100 -0.46700300 0.84834900
C 1.16089400 1.32479100 0.47343200
H 0.93189700 1.29343600 1.53755100
H 2.08027500 1.87606900 0.30307200
H 0.33072700 1.81694000 -0.02966100
O -1.89057300 -0.51398200 -0.01198200
O -1.93594200 0.70410200 -0.78203200
H -2.49077700 1.26291700 -0.21606200

10m

C -1.32842500 -0.10636700 0.07552300
O -2.21446300 -0.63305700 0.67915100
O -0.26261100 -0.93897300 -0.24678400
O 0.82231800 -0.22229900 -0.93978600
C -1.27423800 1.32143600 -0.37631000
H -1.15870200 1.37801200 -1.45823000
H -2.20053000 1.79974900 -0.07385000
H -0.42012700 1.83142400 0.06577500
O 1.95074300 -0.36627500 -0.17275500
O 1.92398800 0.61486800 0.88510700
H 1.63554400 0.06629200 1.63156200

10n

C 1.32391300 0.15594000 -0.02778900
O 1.32097200 1.32586500 -0.24491400
O 0.24650500 -0.55519500 0.48444900
O -0.86052700 0.32285300 0.80471400
C 2.45850800 -0.81352900 -0.22686900
H 2.10368600 -1.76192700 -0.62493100
H 3.18332700 -0.36385600 -0.89904600
H 2.93381800 -1.00844900 0.73530400
O -1.63792700 0.47854500 -0.33572600
O -2.52764100 -0.64052300 -0.43831100
H -3.24641700 -0.37260000 0.15492600

TS-10be

C 1.26385100 0.29798500 0.12649000
O 1.13263100 1.45993000 -0.08479400
O 0.19997800 -0.45063400 0.72115200
O -0.68045400 -0.87520800 -0.36947300
C 2.47207000 -0.54838500 -0.11001900
H 2.77548300 -1.01951900 0.82574900
H 2.21364400 -1.35288300 -0.80054200
H 3.28251500 0.05122500 -0.51325800
O -1.57758000 0.14717000 -0.65482600
O -2.62622400 0.10851800 0.31258300
H -2.27398800 0.70537600 0.99208800

TS-10bk

C -1.13220700 0.16022000 -0.10569800
O -0.76438300 1.18028000 -0.61580700
O -0.35874400 -0.95682100 0.06313600
O 0.95679500 -0.79654200 -0.64868200
C -2.50866900 -0.12218600 0.43534200
H -2.48051900 -0.83355900 1.25710900
H -2.95477800 0.81598000 0.75366200
H -3.11444000 -0.54735900 -0.36616000
O 1.91546900 -0.48765900 0.23927900
O 1.87546600 0.94112600 0.53879400
H 1.39817700 1.29366300 -0.23622700

TS-10bm

C 1.12952500 0.25847100 -0.19449800
O 0.91782400 1.41473300 -0.39387400
O 0.28933000 -0.72575500 -0.78950700
O -0.73348900 -1.08768300 0.19946400
C 2.25046500 -0.33648600 0.58856800
H 2.83328600 -0.99489300 -0.05686700
H 2.88055300 0.44157100 1.00833500
H 1.83327900 -0.95904900 1.38210300
O -1.89583600 -0.40290200 -0.11907100
O -1.88248400 0.87255500 0.52979900
H -1.38982000 1.41287400 -0.11247500

TS-10bn

C 1.26385100 0.29798500 0.12649000
O 1.13263100 1.45993000 -0.08479400
O 0.19997800 -0.45063400 0.72115200
O -0.68045400 -0.87520800 -0.36947300
C 2.47207000 -0.54838500 -0.11001900
H 2.77548300 -1.01951900 0.82574900
H 2.21364400 -1.35288300 -0.80054200
H 3.28251500 0.05122500 -0.51325800
O -1.57758000 0.14717000 -0.65482600
O -2.62622400 0.10851800 0.31258300
H -2.27398800 0.70537600 0.99208800

TS-10ej

C 1.41340300 -0.21083400 -0.03835100
O 2.24496100 -1.02152400 -0.31257800
O 0.21118100 -0.74045100 0.41887900
O -0.79118200 0.30045200 0.78084900
C 1.54378700 1.27901400 -0.13063700
H 1.35509400 1.74630400 0.83475600
H 2.55196500 1.50239800 -0.46466400
H 0.82134700 1.68411700 -0.83845800
O -1.54656200 0.57899800 -0.31066300
O -2.62659300 -0.40681400 -0.42702000
H -2.40598100 -1.02718000 0.28656700

TS-10in

C 1.32560300 0.15137600 -0.02615600
O 1.33034700 1.32602000 -0.21585200
O 0.24166300 -0.56541200 0.45488600
O -0.89604800 0.34391300 0.78180400
C 2.46252800 -0.81604100 -0.23238500
H 2.11335200 -1.76056400 -0.64418100
H 3.18870700 -0.35568800 -0.89607800
H 2.93421100 -1.01970800 0.72967100
O -1.64054600 0.51604300 -0.32416100
O -2.61778700 -0.58141500 -0.43342200
H -2.30609700 -1.18925500 0.25579300

TS-10jl

C 1.49591100 -0.22690700 0.02351500
O 2.29166400 -1.12089900 0.05332200
O 0.19459200 -0.59781200 -0.20492500
O -0.72365200 0.59781500 -0.22515000
C 1.78843800 1.23246800 0.20930300
H 1.23383700 1.62920400 1.05951300
H 2.85506400 1.34368900 0.37647200
H 1.48637700 1.79856500 -0.67159200
O -1.93399700 0.11125100 -0.59017300
O -2.61153800 -0.39301400 0.58079300
H -3.01791900 0.41643500 0.92776600

TS-10kl

C -1.35973600 -0.00111300 0.01768100
O -2.26934500 -0.53613000 -0.52712700
O -0.36594600 -0.81876200 0.65735500
O 0.73765000 -1.01035300 -0.27533300
C -1.16230200 1.46339200 0.23118400
H -0.17672300 1.76381500 -0.11771300
H -1.94371600 2.02086900 -0.27659300
H -1.19425900 1.66633500 1.30329100
O 1.88067500 -0.42449700 0.24753200
O 2.01447600 0.91738200 -0.26440400
H 2.46684200 0.75418800 -1.10635500

TS-10lm

C -1.13220700 0.16022000 -0.10569800
O -0.76438300 1.18028000 -0.61580700
O -0.35874400 -0.95682100 0.06313600
O 0.95679500 -0.79654200 -0.64868200
C -2.50866900 -0.12218600 0.43534200
H -2.48051900 -0.83355900 1.25710900
H -2.95477800 0.81598000 0.75366200
H -3.11444000 -0.54735900 -0.36616000
O 1.91546900 -0.48765900 0.23927900
O 1.87546600 0.94112600 0.53879400
H 1.39817700 1.29366300 -0.23622700

TS-11b

C 1.15433500 0.03799500 -0.00655400
O 0.57623300 1.12812600 0.21936100
C 2.66965200 0.03364700 -0.07050000
H 3.04590300 0.24769300 0.93019800
H 3.05243700 -0.92364600 -0.40825700
H 2.99245600 0.83372000 -0.73380800
O 0.60519000 -1.08913700 -0.19177800
O -1.27463000 -1.00808900 0.44877200
O -1.99426400 -0.30478800 -0.30275300
O -1.82721000 1.06011700 -0.10519800
H -0.71728300 1.12254600 0.12695000

12

C 1.39569100 -0.05927100 -0.07370900
O 0.98003500 1.10429700 0.45692200
O 0.63776800 -0.86539600 -0.55974100
O -1.89481200 -0.79592900 0.79463200
C 2.88727200 -0.22075600 0.01647600
H 3.18174700 -1.16286200 -0.43402900
H 3.38034900 0.60881800 -0.49018500
H 3.19668500 -0.19307500 1.06148100
O -2.31951600 -0.21057900 -0.22128300
O -1.83700100 0.92873800 -0.48892100
H 0.01164800 1.13824200 0.35326100

13

C -1.39133300 -0.12538700 -0.00000300
H -1.66778300 -0.70890700 0.87810900
H -1.66773000 -0.70971900 -0.87758600
H -1.92133000 0.82122800 -0.00042800
C 0.08948000 0.12668400 -0.00002500
O 0.62391500 1.20456100 0.00000500
O 0.79326000 -1.03235000 -0.00000100
H 1.73056100 -0.78806400 0.00003800

14

O 1.07736700 -0.21471600 0.00000000
O 0.00000000 0.43053300 0.00000000
O -1.07736700 -0.21581700 0.00000000

TS-15b (ωB97X-D/cc-pVTZ+d)

C 1.50994500 0.06657200 -0.05793100
O 0.77127300 0.99401900 0.21061800
O 1.00767000 -0.99579500 -0.60840500
O -1.73366000 -1.01250100 0.52249600
C 2.98458500 0.01407700 0.19603900
H 3.44580300 -0.86088900 -0.25717000
H 3.43092000 0.92294100 -0.20271400
H 3.13927000 -0.01010700 1.27394900
O -2.54192600 -0.24017600 -0.04906400
O -1.99500500 1.06895600 -0.27649400
H -1.04998700 0.94814100 -0.03591400

TS-15e (ωB97X-D/cc-pVTZ+d IRCMax geometry)

C 1.52457100 -0.10111000 -0.02876000
O 2.49966000 -0.81179400 0.21053300
O 0.60370700 -0.77195400 -0.60102500
O -1.34572100 0.55564700 -0.86660800
C 1.38917400 1.34437000 0.29466900
H 0.53612300 1.48567200 0.95673100
H 2.30275600 1.69713300 0.76585500
H 1.19330900 1.90544300 -0.61765600
O -2.17451700 -0.21652900 -0.35368600
O -2.06557900 -0.19195400 1.11565400
H -1.65505800 -1.05514400 1.26066600

TS-15l (ωB97X-D/cc-pVTZ+d IRCMax geometry)

C 1.51277000 -0.05306900 -0.04841900
O 2.54433100 -0.39235400 -0.59928200
O 0.65488900 -1.01922400 0.03136400
O -1.20190000 -0.40242200 0.91544700
C 1.20748800 1.30374400 0.49306900
H 0.95247800 1.23528800 1.54919000
H 2.07848700 1.93855100 0.35584100
H 0.34756600 1.71807800 -0.03046000
O -2.04273600 -0.53287000 0.00480800
O -2.06130900 0.65896600 -0.85587600
H -2.84629000 1.10726100 -0.51416100

16b

C 1.59455200 -0.17967200 -0.04582700
O 0.77105100 -0.92381600 -0.63892200
O 2.11056000 -0.77224800 0.93614100
O -1.51128400 1.10440400 0.40973400
C 1.90779900 1.21666900 -0.43885300
H 2.79008000 1.57433600 0.08800200
H 2.06141100 1.26719500 -1.51633800
H 1.05052600 1.84309000 -0.18793500
O -2.49231900 0.35864700 0.14594700
O -2.10194000 -1.01330700 -0.24977500
H -1.12466900 -0.93603500 -0.30064800

16e

C 1.89286500 -0.02514300 -0.06627500
O 3.09217800 -0.43790500 -0.09425600
O 1.08519000 -0.96988300 -0.17992500
O -3.37123600 0.39912200 -0.21820900
C 1.53552500 1.41191900 0.06671300
H 0.59823700 1.50799700 0.61255700
H 2.33329500 1.95801600 0.56701300
H 1.39834900 1.83010100 -0.93215300
O -2.33138700 -0.23764500 -0.43825300
O -1.49815500 -0.35539800 0.84110100
H -0.71292800 -0.80309600 0.46628700

17

C -1.38568500 0.00002300 -0.00304900
H -1.76126200 0.89527500 -0.49555900
H -1.73445800 -0.00086600 1.03086400
H -1.76126400 -0.89442200 -0.49703000
C 0.10337700 0.00000600 -0.00722300
O 0.80944600 1.03866800 0.00146000
O 0.80940800 -1.03868800 0.00146000

18

O 1.17716800 0.10291000 0.00018300
H 0.91246800 1.03967500 -0.00106800
O -0.18188400 -0.53701300 -0.00016100
O -1.10934200 0.30414400 0.00011100

TS-19

O -1.12654100 -0.82811700 0.00000000
H -0.41236000 -1.48772700 0.00000000
O 0.00000000 0.63651800 0.00000000
O 1.17808600 0.37756400 0.00000000

20

O 0.00000000 0.00000000 0.10829200
H 0.00000000 0.00000000 -0.86633600

References

1. M. K. Sprague and K. K. Irikura, *J. Phys. Chem. A*, 2015, **119**, 7052-7062.
2. Y. Georgievskii and S. J. Klippenstein, *J. Chem. Phys.*, 2005, **122**, 194103.