An Experimental and Computational Study of the Reaction Between 2-Methylallyl Radicals and Oxygen Molecules: Optimizing Master Equation Parameters with Trace Fitting

Timo T. Pekkanen[a], Raimo S. Timonen[a], Struan H. Robertson[b], György Lendvay[c], Satya P. Joshi[a], Timo T. Reijonen[a], Arkke J. Eskola[a,*]

[a]*Department of Chemistry, University of Helsinki, P.O. Box 55 (A.I. Virtasen aukio 1), 00014 Helsinki, Finland*
[b]*Dassault Systèmes, 334 Science Park, Cambridge CB4 0WN, U.K.*
[c]*Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar Tudósok krt. 2., Budapest H-1117, Hungary*

Supplemental Material

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*Corresponding author:
Email address: `arkke.eskola@helsinki.fi` (Arkke J. Eskola)

Table S1: The Experimental Conditions and Results of $CH_2C(CH_3)CH_2^{\bullet}$+$O_2$ Bimolecular Rate Coefficient Measurements.

T (K)	p_M (Torr)	[M] (cm^{-3}) 10^{16}	[Pr][a] (cm^{-3}) 10^{12}	[O_2] (cm^{-3}) 10^{13}	k'[b] (s^{-1})	k_w[c] (s^{-1})	k_w[d] (s^{-1})	k_f[e] (cm^3 s^{-1}) 10^{-14}
203[g,l,o]	0.20	0.966	12.5	3.40 − 8.53	53.9 − 105	14.8 ± 1.1	15.2 ± 2.5	108 ± 5
203[g,l,o]	0.37	1.77	20.0	2.94 − 10.3	55.5 − 144	14.9 ± 0.9	16.3 ± 2.5	122 ± 4
203[g,n,o]	0.39	1.84	4.26	1.93 − 5.05	32.1 − 77.3	7.52 ± 0.87	6.73 ± 1.25	140 ± 4
203[g,l,o]	0.77	3.68	18.7	3.42 − 9.78	81.6 − 180	16.3 ± 0.9	17.6 ± 2.8	168 ± 5
203[g,n,o]	0.78	3.69	4.25	1.98 − 4.14	40.6 − 81.7	5.79 ± 0.74	5.55 ± 1.30	178 ± 5
203[g,l,o]	1.30	6.19	17.3	2.86 − 10.1	64.6 − 177	19.0 ± 0.7	21.1 ± 2.7	155 ± 4
203[g,n,o]	1.32	6.30	4.41	1.61 − 3.64	39.1 − 82.0	8.89 ± 0.73	8.09 ± 1.07	197 ± 5
203[h,l,o]	2.26	10.8	33.1	1.52 − 6.68	47.3 − 134	19.5 ± 1.7	21.0 ± 5.0	182 ± 14
203[h,l,o]	3.17	15.1	31.0	1.01 − 4.51	40.8 − 112	20.6 ± 1.7	19.5 ± 2.3	196 ± 10
203[h,l,o]	4.31	20.5	60.3	1.25 − 3.50	44.8 − 85.1	20.5 ± 1.8	21.0 ± 2.0	193 ± 10
203[h,l,o]	6.29	29.9	66.1	2.06 − 9.03	71.8 − 235	19.8 ± 1.3	21.6 ± 2.6	238 ± 6
220[g,l,o]	0.85	3.73	35.5	3.32 − 8.46	44.5 − 111	6.81 ± 1.44	7.58 ± 5.39	122 ± 10
243[g,l,o]	0.25	0.981	21.8	5.29 − 20.8	36.0 − 113	7.83 ± 1.00	11.0 ± 6.6	53.0 ± 5.0
243[g,l,o]	0.46	1.81	22.1	5.14 − 14.9	46.7 − 133	7.64 ± 1.07	5.29 ± 1.87	84.6 ± 2.1
243[g,l,o]	0.95	3.78	22.6	2.31 − 8.74	35.6 − 113	5.16 ± 0.76	6.17 ± 2.32	122 ± 4
243[g,n,o]	1.58	6.27	4.12	1.84 − 5.83	27.2 − 82.1	3.19 ± 0.70	2.42 ± 1.27	136 ± 4
243[g,l,o]	1.61	6.38	23.9	2.87 − 11.8	41.6 − 144	4.83 ± 0.89	7.88 ± 5.24	119 ± 8
233[h,l,o]	2.69	11.1	54.0	1.61 − 4.72	36.7 − 81.1	11.3 ± 0.9	11.4 ± 2.40	154 ± 9
233[h,l,o]	3.84	15.9	54.5	1.53 − 5.26	60.0 − 106	12.1 ± 1.3	12.3 ± 1.6	174 ± 5
243[h,l,o]	5.16	20.5	44.3	2.03 − 4.63	47.2 − 94.0	9.54 ± 1.19	9.61 ± 0.95	182 ± 3
243[h,l,o]	7.60	30.2	64.3	3.70 − 5.40	83.0 − 115	10.6 ± 0.7	10.8 ± 0.3	194 ± 8
266[d,k,o]	1.04	3.78	13.8	7.19 − 12.8	51.6 − 105	7.03 ± 0.60	6.41 ± 1.49	74.7 ± 1.9
298[g,l,o]	0.27	0.883	7.15	12.8 − 35.3	41.4 − 105	7.98 ± 0.75	7.11 ± 1.47	27.4 ± 0.7
303[i,l,o]	0.57	1.81	3.25	8.57 − 29.2	41.1 − 107	10.1 ± 1.33	11.4 ± 3.3	34.9 ± 2.0
298[j,m,o]	0.57	1.84	4.69	10.9 − 32.6	42.6 − 121	8.11 ± 0.30	7.31 ± 1.45	34.2 ± 0.8
298[g,n,o]	0.57	1.85	7.95	7.39 − 32.1	36.4 − 132	4.43 ± 1.58	4.62 ± 5.17	37.4 ± 2.7
298[g,l,o]	0.57	1.85	7.95	8.71 − 29.2	34.5 − 116	5.03 ± 0.80	4.51 ± 3.89	37.1 ± 2.1
298[g,l,o]	1.17	3.79	9.01	6.37 − 16.5	38.7 − 86.7	7.14 ± 0.55	8.20 ± 1.83	48.7 ± 1.8
298[g,l,o]	1.98	6.40	7.72	4.28 − 12.9	31.2 − 86.7	6.36 ± 0.54	5.49 ± 0.83	62.6 ± 1.1
304[k,l,o]	2.86	9.09	3.75	7.29 − 26.3	64.8 − 192	12.0 ± 0.6	13.5 ± 1.9	68.3 ± 1.3
298[h,l,o]	3.39	11.0	28.5	4.04 − 12.9	52.3 − 115	15.5 ± 1.2	19.7 ± 3.7	76.6 ± 5.4
298[h,m,o]	4.69	15.2	12.6	4.01 − 15.5	47.7 − 147	6.87 ± 0.92	8.72 ± 1.76	90.5 ± 1.9
298[h,l,o]	6.38	20.7	42.7	3.64 − 9.19	46.4 − 98.4	6.20 ± 0.83	6.81 ± 2.53	103 ± 5
298[h,m,o]	9.23	29.9	28.1	3.79 − 8.83	60.3 − 120	9.42 ± 0.72	10.4 ± 1.3	126 ± 3
304[k,l,p]	0.88	2.78	4.43	5.77 − 18.8	43.0 − 125	12.1 ± 0.8	11.7 ± 3.5	62.7 ± 3.3
304[k,l,p]	0.92	2.92	9.81	8.73 − 22.4	81.0 − 176	22.7 ± 0.7	22.4 ± 1.1	68.6 ± 0.9
304[k,l,p]	1.38	4.38	7.73	4.23 − 17.0	46.6 − 146	13.2 ± 0.7	13.4 ± 1.2	77.3 ± 1.3
304[k,l,p]	1.88	5.96	7.19	6.76 − 12.2	67.5 − 121	12.6 ± 0.9	11.5 ± 2.2	88.3 ± 2.9
304[k,l,p]	1.90	6.04	8.99	8.26 − 19.3	86.9 − 191	18.2 ± 1.0	17.7 ± 4.0	87.2 ± 3.5

[a] Radical precursor used was 3-bromo-2-methylpropene kept at around −7 °C. KrF (248 nm) laser used for photolysis.
[b] The pseudo first-order rate coefficient $k' = k[O_2] + k_w$.
[c] Average of measured wall rates. Stated uncertainty is the average standard error (1σ) of the fits. Wall rate is the radical decay rate in the absence of added oxygen.
[d] Wall rate determined from the linear fit y-axis intercept of the bimolecular plot. Stated uncertainty is the standard error (1σ) of the fit.
[e] Experimentally determined bimolecular rate coefficient (slope of the bimolecular plot). Stated uncertainty is the standard error (1σ) of the linear fit. Estimated overall uncertainty is ±15 %.
[f] Bimolecular rate coefficient calculated by our master equation model.
[g] Reactor: $d = 1.7$ cm, stainless steel, halocarbon wax coating.
[h] Reactor: $d = 0.8$ cm, stainless steel, halocarbon wax coating.
[i] Reactor: $d = 1.70$ cm, quartz, boric oxide coating
[j] Reactor: $d = 1.65$ cm, Pyrex, polydimethylsiloxane coating.
[k] Reactor: $d = 0.85$ cm, quartz, boric oxide coating
[l] Detection: chlorine lamp with a CaF_2 window.
[m] Detection: chlorine lamp with a BaF_2 window.
[n] Detection: xenon lamp with a sapphire window.
[o] He used as buffer gas.

[p] N_2 used as buffer gas.

Table S2: The Experimental Conditions and Results of $CH_2C(CH_3)CH_2^{\bullet} + O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_2C(CH_3)CH_2OO^{\bullet}$ Equilibrium Constant Measurements.

T (K)	p (Torr)	[M] (cm^{-3}) 10^{16}	[O_2] (cm^{-3}) 10^{14}	k_w[a] (s^{-1})	k_p[b] (s^{-1})	k_f[c] ($cm^3\ s^{-1}$) 10^{-14}	k_r[d] (s^{-1})	ln(K)[e]	$f(T)$[f] 10^{-4}
347[g,j]	0.69	1.92	4.58	6.83 ± 0.45	19.8 ± 3.3	18.7 ± 2.0	19.9 ± 9.4	12.19 ± 0.49	−7.382
351[h,k]	0.71	1.96	5.84	12.3 ± 0.5	26.3 ± 5.5	16.9 ± 1.9	14.6 ± 12.2	12.39 ± 0.85	−8.353
351[h,k]	0.74	2.03	10.8	11.5 ± 0.6	28.5 ± 5.4	17.6 ± 1.7	17.5 ± 15.8	12.24 ± 0.91	−8.3533
354[g,j]	0.69	1.89	2.53	8.25 ± 0.37	23.6 ± 8.5	14.0 ± 3.1	18.0 ± 16.1	11.98 ± 0.92	−9.528
354[g,j]	0.70	1.92	5.20	6.81 ± 0.42	18.4 ± 3.7	17.4 ± 2.1	24.5 ± 12.6	11.88 ± 0.53	−9.528
357[h,k]	0.74	2.00	9.13	11.8 ± 0.7	28.9 ± 4.8	16.3 ± 1.7	21.3 ± 14.9	11.95 ± 0.71	−10.25
358[g,j]	0.71	1.92	5.49	7.14 ± 0.39	18.2 ± 2.6	16.6 ± 1.8	34.0 ± 10.8	11.50 ± 0.33	−10.29
363[g,k]	0.54	1.43	13.1	7.59 ± 0.64	14.4 ± 4.5	10.5 ± 1.4	21.3 ± 17.4	11.50 ± 0.83	−12.37
363[g,j]	0.73	1.93	6.15	7.06 ± 0.38	17.4 ± 2.1	15.7 ± 1.6	43.7 ± 10.9	11.18 ± 0.27	−12.37
368[h,k]	0.77	2.01	9.18	11.6 ± 0.5	20.8 ± 1.5	13.8 ± 1.2	36.8 ± 7.0	11.21 ± 0.21	−14.12
368[g,j]	0.73	1.92	6.66	6.59 ± 0.37	16.6 ± 1.7	16.4 ± 1.6	63.7 ± 12.1	10.83 ± 0.22	−14.12
368[g,k]	0.74	1.94	6.74	5.92 ± 0.31	19.5 ± 2.4	18.4 ± 2.0	69.6 ± 17.8	10.86 ± 0.28	−14.12
373[g,k]	0.75	1.95	7.41	6.60 ± 0.28	15.1 ± 2.1	15.2 ± 1.8	73.3 ± 18.3	10.60 ± 0.28	−15.99
373[h,k]	0.78	2.06	9.03	10.2 ± 0.4	23.3 ± 2.5	11.7 ± 1.1	46.0 ± 10.8	10.80 ± 0.25	−15.99
378[g,k]	0.77	1.96	8.44	6.20 ± 0.37	14.5 ± 1.9	14.4 ± 1.6	80.9 ± 18.9	10.43 ± 0.26	−18.14
379[i,k]	3.65	9.30	2.58	9.95 ± 0.50	16.1 ± 4.9	16.5 ± 3.3	140 ± 36	10.02 ± 0.32	−18.47
383[g,k]	0.78	1.97	9.15	6.68 ± 0.38	13.5 ± 2.0	14.2 ± 1.8	116 ± 26	10.04 ± 0.26	−20.32
389[g,k]	0.80	1.98	10.7	6.15 ± 0.38	13.6 ± 2.8	13.0 ± 2.1	158 ± 45	9.635 ± 0.327	−23.06
393[g,k]	0.86	2.11	11.5	8.17 ± 0.25	11.8 ± 1.2	12.3 ± 1.2	157 ± 19	9.573 ± 0.154	−25.01
394[h,l]	0.57	1.40	12.0	10.2 ± 0.8	26.1 ± 5.3	9.21 ± 1.57	118 ± 36	9.572 ± 0.347	−25.90
394[h,k]	0.57	1.41	12.2	11.7 ± 1.1	24.0 ± 5.4	8.43 ± 1.48	96.0 ± 33.1	9.689 ± 0.387	−25.90
398[g,k]	0.45	1.09	10.4	6.81 ± 0.59	14.0 ± 3.1	8.15 ± 1.57	163 ± 34	9.115 ± 0.285	−27.68
398[g,k]	0.81	1.97	10.4	5.45 ± 0.31	12.7 ± 3.7	9.26 ± 2.02	201 ± 56	9.034 ± 0.356	−27.68
398[g,k]	1.23	2.98	10.2	6.33 ± 0.29	12.1 ± 3.3	10.9 ± 2.1	279 ± 66	8.868 ± 0.308	−27.68
403[g,k]	0.83	1.98	9.70	4.67 ± 0.40	12.0 ± 3.8	7.81 ± 1.78	249 ± 61	8.637 ± 0.335	−30.02
409[g,k]	0.86	2.03	11.3	4.06 ± 0.43	30.4 ± 11.1	7.39 ± 2.13	353 ± 105	8.219 ± 0.415	−33.97
409[g,k]	0.87	2.04	12.1	4.06 ± 0.43	17.3 ± 5.1	7.75 ± 1.71	273 ± 71	8.523 ± 0.340	−33.97
410[h,k]	1.17	2.75	14.7	12.5 ± 0.8	25.1 ± 13.1	6.12 ± 2.27	327 ± 148	8.104 ± 0.585	−34.82
384[i,k,m]	1.75	4.41	7.80	20.5 ± 0.9	18.0 ± 5.5	25.6 ± 5.2	221 ± 87	9.989 ± 0.441	−20.84

[a] Average of measured wall rates. Stated uncertainty is the average standard error (1σ) of the fits.

[b] Irreversible first order loss rate for $CH_2C(CH_3)CH_2OO^{\bullet}$. Propagation of error used to obtain the uncertainty.

[c] The bimolecular rate coefficient for the forward reaction. Propagation of error used to obtain the uncertainty.

[d] Unimolecular rate coefficient for the reverse reaction. Propagation of error used to obtain the uncertainty.

[e] Gases are assumed to be ideal and the standard state has been chosen as pure gas at 1 bar ($p^{\ominus} = 1$ bar) at the temperature of interest. Propagation of error used to obtain the uncertainty. Estimated overall uncertainty is ±15 %.

[f] Value of the correction function [see equation (21) in main text].

[g] Reactor: $d = 1.65$ cm, Pyrex, polydimethylsiloxane coating.

[h] Reactor: $d = 1.70$ cm, quartz, boric oxide coating

[i] Reactor: $d = 0.85$ cm, quartz, boric oxide coating

[j] Detection: chlorine lamp with a BaF_2 window.

[k] Detection: chlorine lamp with a CaF_2 window.

[l] Detection: xenon lamp with a sapphire window.

[m] N_2 used as buffer gas.

Table S3: Values of the Fit Parameters for the Double Exponential Fitting Function $[\mathrm{R}^\bullet](t) = A + B\mathrm{e}^{-\lambda_1 t} + C\mathrm{e}^{-\lambda_2 t}$.

T (K)	p (Torr)	λ_1 (s^{-1})	λ_2 (s^{-1})	A	B	C
347	0.69	114.9877 ± 6.422	17.0742 ± 2.1999	1461.6111	1470.1227 ± 41.5486	441.1227 ± 50.5904
351	0.71	127.7201 ± 6.9466	24.3262 ± 4.0719	94.1912	434.0637 ± 13.7207	82.8483 ± 16.2968
351	0.74	221.3157 ± 8.8555	26.9365 ± 4.4958	100.6765	444.635 ± 9.6231	48.3591 ± 7.9139
354	0.69	67.8377 ± 11.352	17.3383 ± 3.035	2072.2917	1604.0523 ± 296.5284	1478.4288 ± 323.5545
354	0.70	124.3734 ± 9.1509	15.6997 ± 2.2828	1581.1111	1376.0877 ± 45.4979	459.7239 ± 53.0616
357	0.74	183.8175 ± 9.8338	26.5317 ± 3.5386	65.1944	284.2304 ± 7.203	50.2003 ± 7.0739
358	0.71	135.7581 ± 8.3377	14.9966 ± 1.3316	1600.7037	1412.5415 ± 38.5773	628.4762 ± 40.7403
363	0.54	167.7005 ± 12.0111	13.4157 ± 3.5744	139.4769	291.4314 ± 9.6817	49.0268 ± 7.8894
363	0.73	151.0271 ± 8.8132	14.0054 ± 0.91787	1581.6852	1424.4017 ± 38.8251	746.2006 ± 32.2663
368	0.77	177.6665 ± 5.2369	18.6297 ± 0.87351	269.5692	1194.5538 ± 16.5167	388.3467 ± 14.4145
368	0.73	183.3918 ± 10.1639	12.8033 ± 0.58087	1533.6111	1339.3342 ± 40.1995	877.2237 ± 22.6107
368	0.74	204.4506 ± 14.9105	14.4061 ± 0.67285	898.3148	936.7394 ± 44.7643	606.6284 ± 17.4537
373	0.75	195.9915 ± 15.4997	11.6377 ± 0.65781	1111.8704	943.0978 ± 45.8937	671.6817 ± 19.4814
373	0.78	165.9019 ± 8.6222	19.0793 ± 1.071	164.6769	555.7099 ± 13.6234	289.071 ± 13.4036
378	0.76	211.5434 ± 16.0576	11.0736 ± 0.48362	1260.5556	1137.6324 ± 68.5544	824.8424 ± 17.5058
379	3.65	197.6568 ± 34.5487	11.3522 ± 0.3143	276.5932	228.7532 ± 22.5888	805.5799 ± 11.0855
383	0.78	255.9033 ± 22.7849	10.2197 ± 0.37694	1368.0741	1091.3235 ± 83.2263	1037.3931 ± 16.4603
389	0.80	307.0864 ± 39.5679	9.5802 ± 0.34023	1383.0926	924.9608 ± 120.2193	1107.6658 ± 15.4469
393	0.86	308.6234 ± 16.9510	9.8777 ± 0.21091	2407.3333	3487.5462 ± 182.4596	3971.9217 ± 28.9583
394	0.57	247.4149 ± 31.8409	17.618 ± 0.66557	84.9848	192.3173 ± 16.0448	234.9228 ± 6.0842
394	0.57	216.7614 ± 29.0947	17.8859 ± 0.97031	142.8859	187.0169 ± 13.615	197.1213 ± 7.678
398	0.45	259.5052 ± 32.005	9.2037 ± 0.34721	1599.4386	996.3806 ± 90.0106	2029.3616 ± 25.3044
398	0.81	307.557 ± 52.6672	7.7563 ± 0.30698	1803.0566	951.5655 ± 160.8805	2080.1082 ± 22.7331
398	1.23	400.1305 ± 62.5391	7.9484 ± 0.23043	1988.7736	1180.3892 ± 174.8299	3052.9251 ± 23.524
403	0.83	334.9961 ± 58.9342	6.3457 ± 0.25898	3377.3922	1379.4587 ± 227.8499	4738.3923 ± 36.9004
409	0.86	462.1901 ± 101.85	8.8828 ± 0.19068	2434.7193	1207.866 ± 283.3556	5719.0813 ± 30.6732
409	0.87	380.6822 ± 67.6023	7.3538 ± 0.30174	2189.0189	945.336 ± 145.7007	2953.1675 ± 25.8853
410	1.17	438.9229 ± 143.4582	15.1502 ± 0.43604	190.6154	84.6101 ± 17.502	326.7437 ± 4.9748
384	1.75	440.0191 ± 76.8555	19.3247 ± 0.77223	123.4578	147.5588 ± 19.9137	161.7532 ± 4.1259

Uncertainties are the standard errors (1σ) of the fit. Parameter A is the average signal background.

Table S4: Reaction enthalpies at zero kelvin ($\Delta_r H_0^\ominus$) for the stationary points on the $CH_2C(CH_3)CH_2^\bullet + O_2$ potential energy surface. The enthalpies are reported at various levels of theory. The coupled cluster and CASPT2 energies have been extrapolated to the complete basis set limit (see text for details).

Species	MN15 (kJ mol^{-1})	ROHF-CCSD(T) [a] (kJ mol^{-1})	UHF-CCSD(T) [b] (kJ mol^{-1})	ROHF-DLPNO-CCSD(T1) [c] (kJ mol^{-1})	CASPT2 [d,e] (kJ mol^{-1})	ΔZPE (kJ mol^{-1})
			$CH_2C(CH_3)CH_2^\bullet + O_2 \longrightarrow$ Products			
R	0	0 (0.029, 0.017)	0 (0.025, 0.016; 0.95, 2.0)	0 (0.028, 0.017)		0
P1	-91.27	-79.81 (0.011, 0.013)	-81.25 (0.011, 0.0081; 0, 0.76)	-86.18 (0.011, 0.016)		5.801
P2	-286.0	-287.0 (0.022, 0.015)	-287.5 (0.026, 0.015; 0.89, 0)	-288.8 (0.021, 0.015)		-1.262
P3	-150.8	-135.4 (0.018, 0.015)	-136.7 (0.016, 0.015; 0.76, 0)	-138.4 (0.017, 0.015)		4.138
P4	-204.9	-212.2 (0.014, 0.013)	-213.6 (0.014, 0.0081; 0, 0.76)	-215.1 (0.013, 0.016)		0.9456
Int1	-94.41	-81.12 (0.025)	-82.53 (0.022, 0.76)	-80.57 (0.023)	**-81.12**[e]	18.86
Int2	-84.48	-70.46 (0.023)	-70.78 (0.022, 0.95)	-72.51 (0.022)	-75.14 (0.78)	14.62
Int3	-95.36	-71.30 (0.015)	-72.66 (0.013, 0.77)	-73.73 (0.014)	-71.11 (0.78)	18.90
Int4	-26.07	-6.445 (0.015)	-7.895 (0.014, 0.76)	-8.177 (0.014)		14.82
Int5	-220.9	-197.2 (0.017)	-198.7 (0.015, 0.76)	-199.1 (0.016)		16.79
Int6	-104.1	-85.15 (0.024)	-85.29 (0.023, 0.95)	-86.14 (0.023)		12.11
TS01	-0.5054	-5.588 (0.047)	-6.736 (0.047, 0.81)	10.12 (0.042)		7.038
TS12A	4.493	21.52 (0.027)	21.90 (0.030, 0.99)	23.30 (0.024)	13.88 (0.77)	4.598
TS12B	9.433	27.81 (0.024)			22.16 (0.77)	4.318
TS13	16.67	32.69 (0.026)	34.09 (0.033, 1.1)	35.07 (0.030)	26.57 (0.78)	15.01
TS14	26.31	40.78 (0.025)	42.22 (0.031, 1.0)	28.70 (0.034)		12.56
TS16	67.13	81.54 (0.027)	81.78 (0.030, 1.0)	82.87 (0.025)		1.917
TS2P1	71.27	66.69 (0.026)	71.66 (0.042, 1.4)	68.31 (0.025)	56.93 (0.77)	7.259
TS35	15.27	13.43 (0.070)	68.65 (0.058, 1.7)	39.24 (0.046)	23.85 (0.78)	8.397
TS45	49.15	48.22 (0.036)	56.71 (0.042, 1.4)	52.11 (0.033)		11.97
TS4P2	47.95	70.34 (0.026)	72.03 (0.029, 1.0)	71.60 (0.024)		9.120
TS5P3	-155.8	-134.3 (0.022)	-134.2 (0.025, 0.89)	-134.0 (0.021)		10.34
TS6P4	-102.7	-95.76 (0.030)	-92.39 (0.039, 1.3)	-92.91 (0.028)		7.256
			$Int2 + O_2 \longrightarrow P5$ (KHP + $OH^\bullet$)			
Int2 + O_2	0			0 (0.022, 0.017)		0
P5	-197.5			-210.8 (0.013, 0.016)		1.085
Int7	-94.11			-81.07 (0.022)		18.75
Int8	-104.6			-87.83 (0.021)		11.24
TS78a	-2.567			17.39 (0.021)		3.629
TS78b	-5.292			12.49 (0.021)		2.141
TS8P5	-103.8			-93.02 (0.023)		8.061

[a] Value in the parentheses is the T1 diagnostic.
[b] Values in the parentheses are the T1 diagnostic and spin contamination, respectively.
[c] Value in the parentheses is the T1 diagnostic.
[d] Value in the parentheses is the reference weight.
[e] The CASPT2 energies here are reported relative to Int1. The relative energy of Int1 has been given its ROHF-CCSD(T) value.

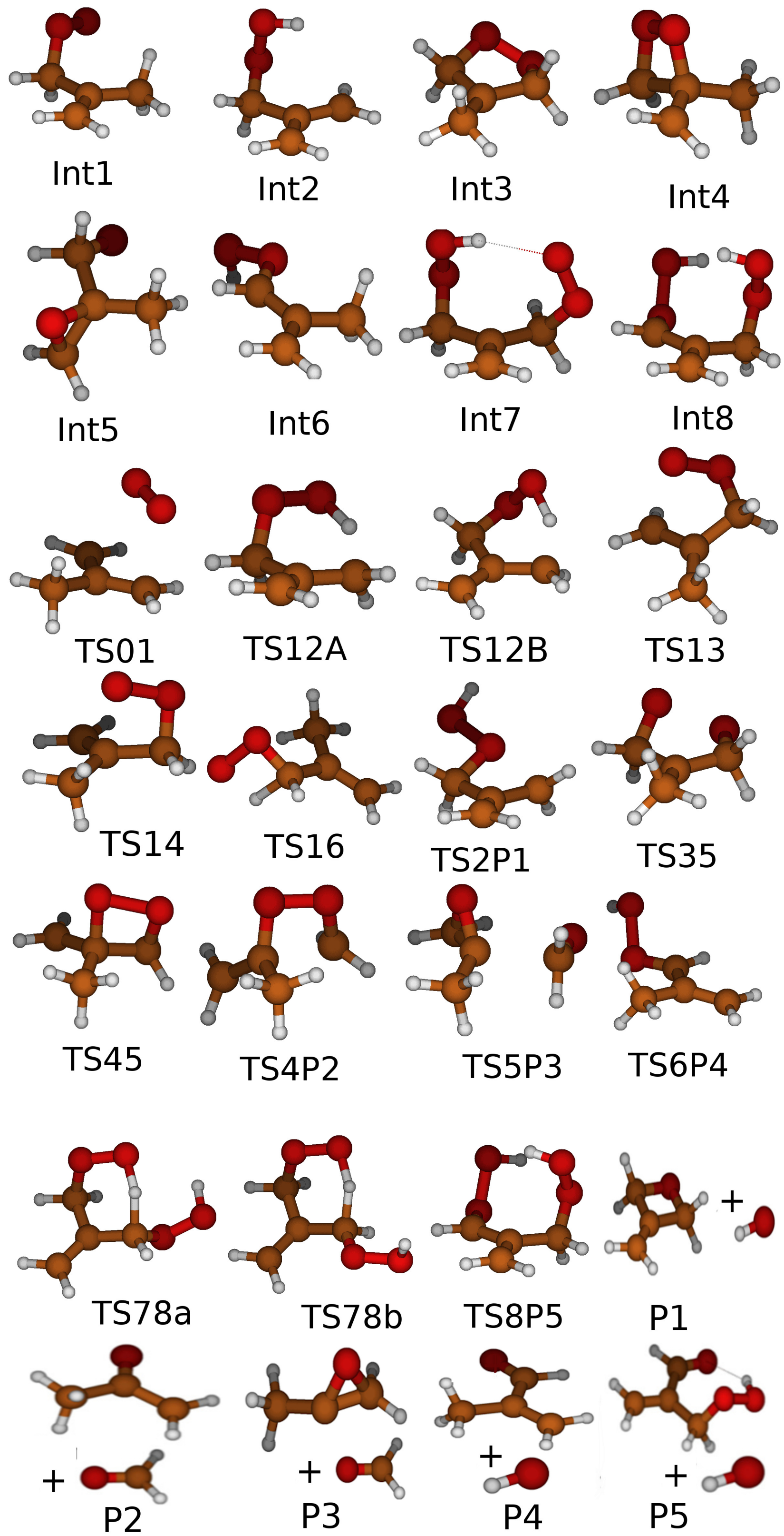

Figure S1: Structures of the stationary points on the $CH_2C(CH_3)CH_2^{\bullet} + O_2$ potential energy surface.