Electronic Supplementary Information

Kinetics of 1- and 2-methylallyl + O_2 reaction, investigated by photoionisation using synchrotron radiation

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Additional experimental information:

For the interpretation of the data it is important to ensure that the reaction mixture is replaced during two laser shots.

The velocity of the gas stream was calculated according to the equation:

$$\frac{0.01*(\text{Total Flow[sccm]})*\frac{T[K]}{298}*\frac{1013.25\ \text{mbar}}{p_R[\text{mbar}]}*\frac{1}{60}}{\pi*(\frac{\text{Reactor I.D.[mm]}}{2})^2} = \text{Flow}\ [\frac{m}{s}]$$

The total flow of the system was set to 50 sccm in all experiments , reactor length was 51 cm, inner diameter (ID) =10 mm, temperature T= 298 K. The flows at 1, 2 and 3 mbar were calculated to be 13.44, 10.75, 5.38 m/s respectively.

As the repetition rate of the laser is 10 Hz, the distance the gas travels between two pulses are 134 cm (1 mbar), 108 cm (2 mbar), and 54 cm (3 mbar) respectively. Thus, the gas is completely replenished between two laser shot.

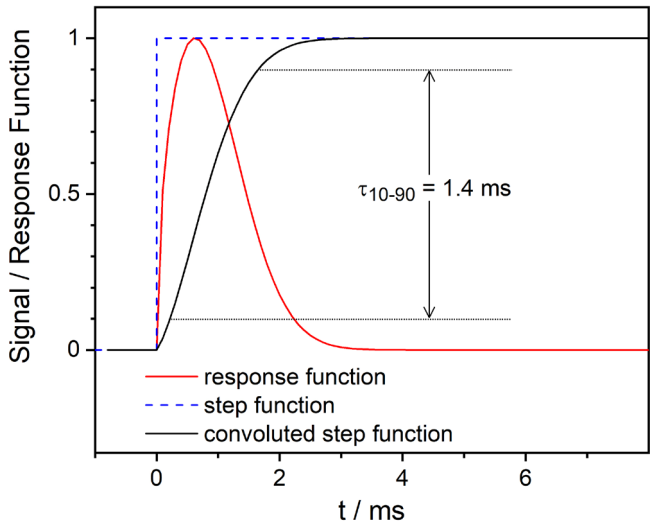


Figure S1: Maxwell-Boltzmann type response function (red curve) used for convolution of the experimental data. As shown by the example step function (blue dashed line), the convoluted function (black curve) exhibits a $\tau_{10\text{-}90}$ rise time of 1.4 ms. The functional form is based on a previous analysis of experimental step-like profiles of HCl (Ref. 43).

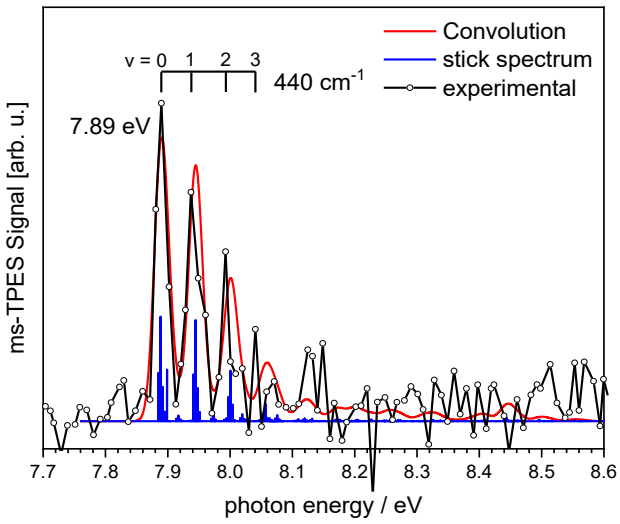


Figure S2: ms-TPES of the 2-MA radical. The radicals were generated at 0.9 mbar by photolysis of 2-methylallyl iodide at 213 nm. Every point was averaged for 390 s, step size is 10 meV.

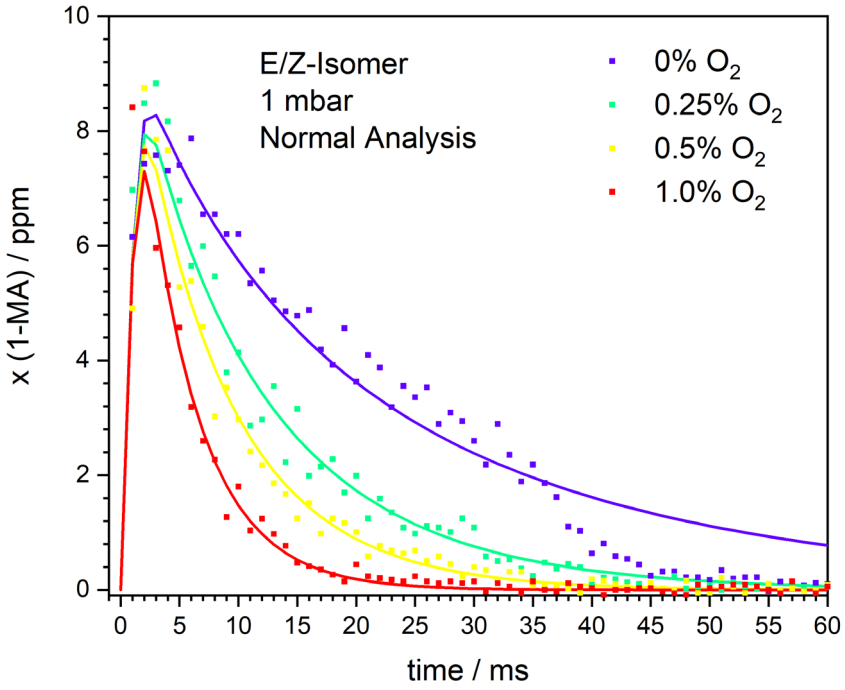


Figure S3: Experimental data (squares) and fitted kinetic traces (lines) for 1-MA at 7.59 eV, collecting all ions. The visible sharp decay at 35 ms in the trace without oxygen is explained by the pump out of the photolyzed mixture.

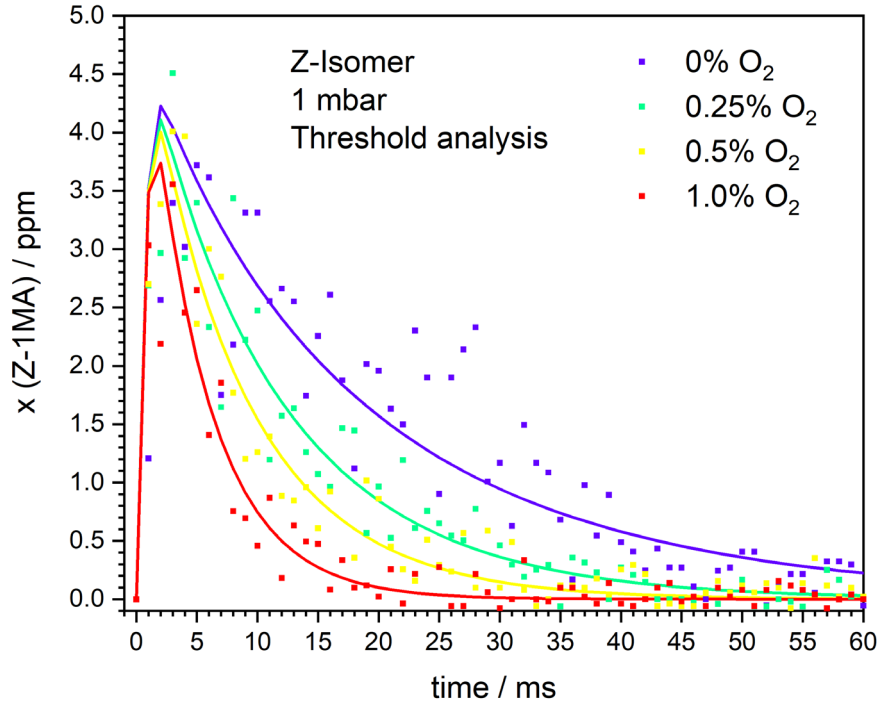


Figure S4: Experimental data (squares) and fitted kinetic traces (lines) for Z-1-MA only using the threshold electron signal for analysis. As visible, the decay is similar, but the signal-to-noise ratio is not good enough to extract accurate rates.

Pseudo-first order analysis

The measured MA concentration time profiles have been additionally analyzed by fitting single-exponential functions to the observed decays with or without taking into account the convolution with the instrument response function as shown in Fig. S1. The results are shown in the pseudo-first order plots in Fig. S5a-S5d, where the resulting y-axis intercepts indicate the influence of the background chemistry. Table S1 compares the corresponding $k2^{nd}$ values from these simple first-order analyses with the k^{2nd} values obtained from the full numerical simulations as described in the main text. Compared to these values, up to 27% too low values have been obtained for the evaluation neglecting the instrument response function (13% deviation on average). In contrast, the pseudo-first order analyses taking into account the instrument response is in better agreement with the full numerical simulation data within 9% on average. The results indicate near pseudo-first-order reaction conditions, but also highlight the importance of a full numerical simulation of the profiles.

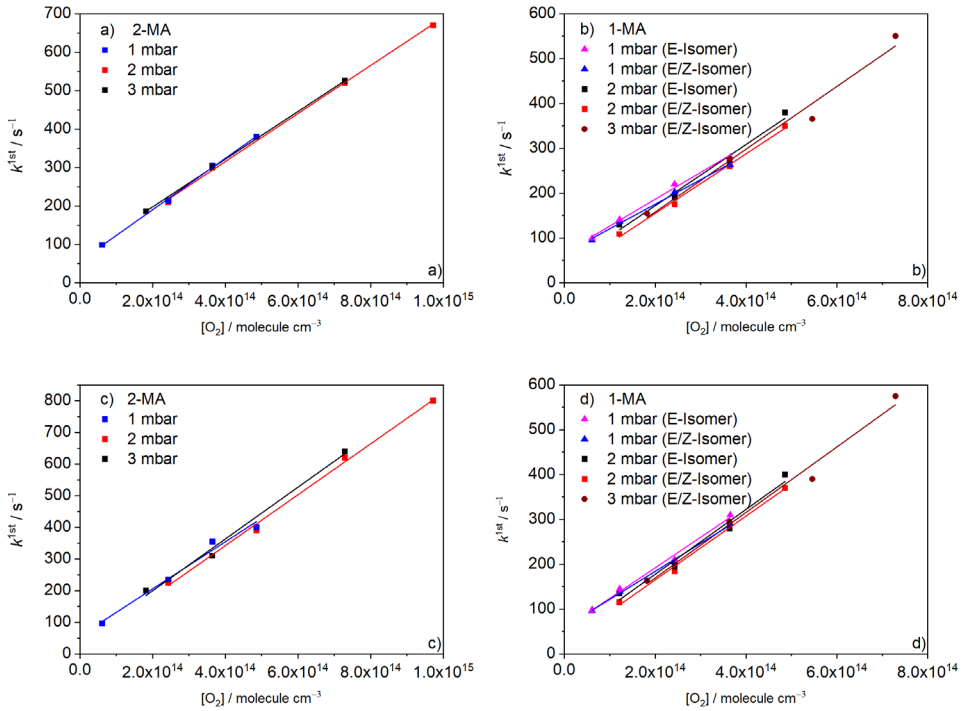


Figure S5: Pseudo-first order plots of the rate constants for the reactions 2-MA (left) and 1-MA + O_2 (right). The upper plots a) and b) correspond to an evaluation directly fitting the decay of the signal with a single-exponential function, the lower plots c) and d) to an evaluation allowing for the convolution with the instrument response function as shown in Fig. S1.

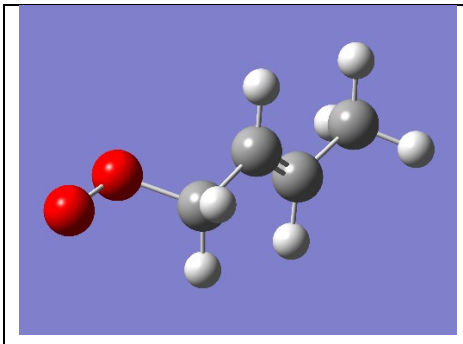
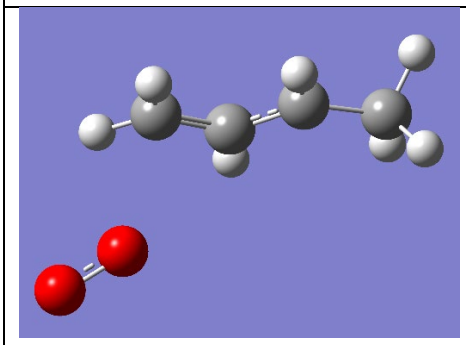
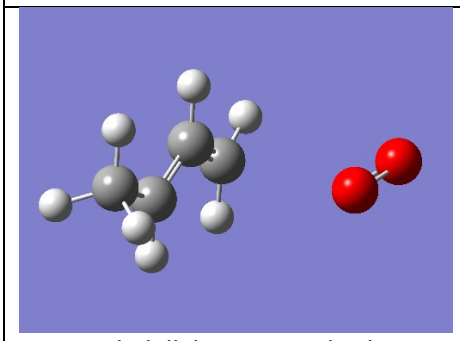
Table S1: Overview of the experimental conditions used to measure the rate coefficient of the reaction $C_4H_7 + O_2$.

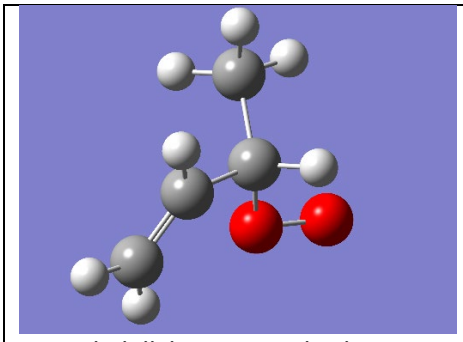
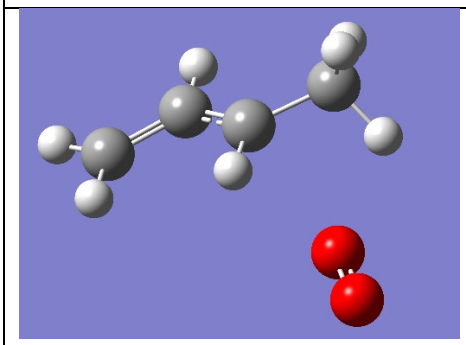
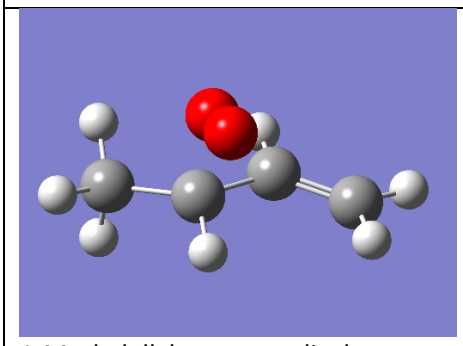
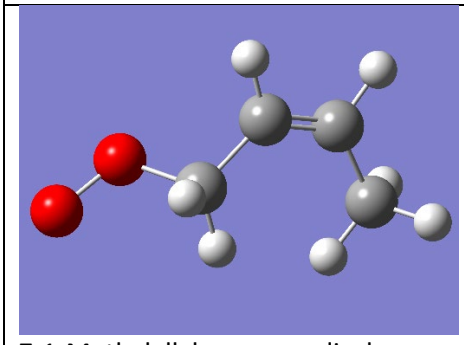
Experiment, precursor	[He]	$[Precursor]_0$	[Radical]	$[O_2]$	p_r	$k_{1/2}$ / $cm^{-3}mol^{-1}s^{-1}$
	/ (molecule cm^{-3})				/ mbar	/ cm^3 mol^{-1} s^{-1}
2-Methylallyl iodide	2.43×10^{16}	8.26×10^{11}	4.45×10^{10}	0	1.0	see Table 1 for background rates
	$2.42 – 2.38 \times 10^{16}$	8.26×10^{11}	4.45×10^{10}	$0.61 – 4.86 \times 10^{14}$	1.0	$5.2 \pm 1.0 \times 10^{11}$
	4.86×10^{16}	8.26×10^{11}	4.45×10^{10}	0	2.0	see Table 1 for background rates
	$4.86 – 4.84 \times 10^{16}$	8.26×10^{11}	4.45×10^{10}	$2.43 – 9.72 \times 10^{14}$	2.0	$5.1 \pm 1.0 \times 10^{11}$
	7.29×10^{16}	8.26×10^{11}	4.45×10^{10}	0	3.0	see Table 1 for background rates
	$7.27 – 7.22 \times 10^{16}$	8.26×10^{11}	4.45×10^{10}	$1.82 – 7.29 \times 10^{14}$	3.0	$5.1 \pm 1.0 \times 10^{11}$
Crotyl bromide	2.43×10^{16}	5.59×10^{12}	2.22×10^{10}	0	1.0	see Table 1 for background rates
	$2.42 – 2.39 \times 10^{16}$	5.59×10^{12}	2.22×10^{10}	$0.61 – 3.65 \times 10^{14}$	1.0	$3.6 \pm 0.7 \times 10^{11}$ (E) $3.4 \pm 0.7 \times 10^{11}$ (E/Z)
	4.86×10^{16}	6.27×10^{12}	2.51×10^{10}	0	2.0	see Table 1
	$4.85 – 4.81 \times 10^{16}$	6.27×10^{12}	2.51×10^{10}	$1.21 – 4.86 \times 10^{14}$	2.0	$3.9 \pm 0.8 \times 10^{11}$ (E) $3.7 \pm 0.8 \times 10^{11}$ (E/Z)
	7.29×10^{16}	6.27×10^{12}	2.51×10^{10}	0	3.0	see Table 1 for background rates
	$7.27 – 7.22 \times 10^{16}$	6.27×10^{12}	2.51×10^{10}	$1.82 – 7.29 \times 10^{14}$	3.0	$4.6 \pm 0.9 \times 10^{11}$ (E/Z)

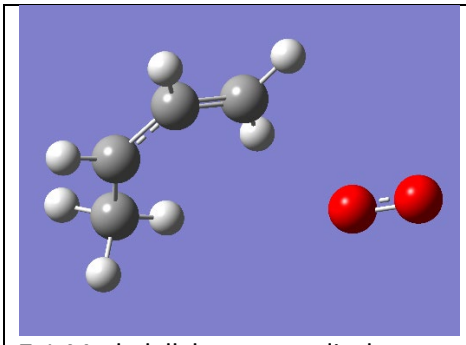
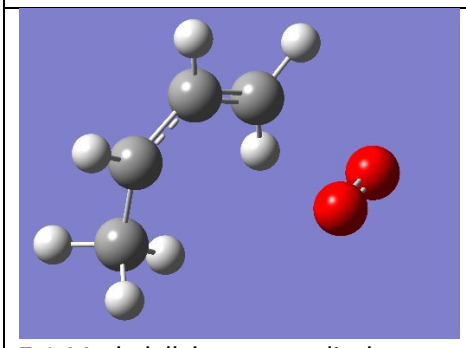
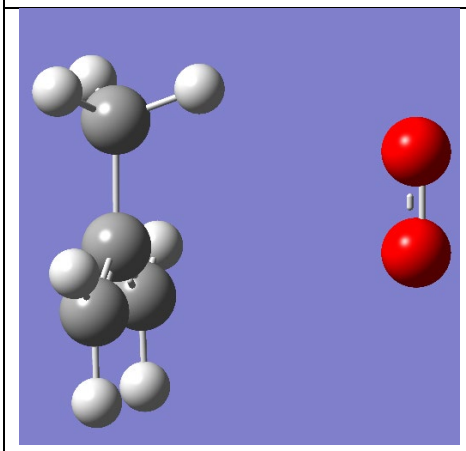
Table S2: Comparion of rate constant data for reaction (1) and (2) from three different evaluations. The first value corresponds to a pseudo-first order analysis neglecting the instrument's response function; the second value to a pseudo-first order analysis taking into account the instrument's reponse function as shown in Figure S1, and the third to the full numerical simulation of the observed decay profiles as described in the main text.

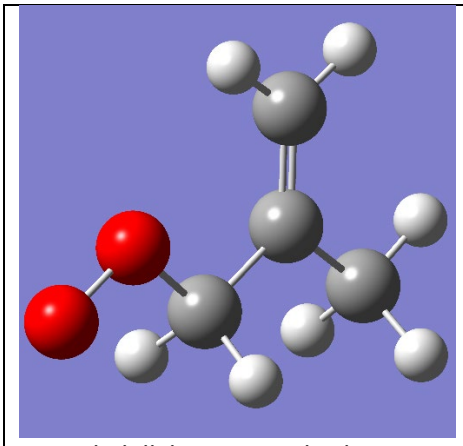
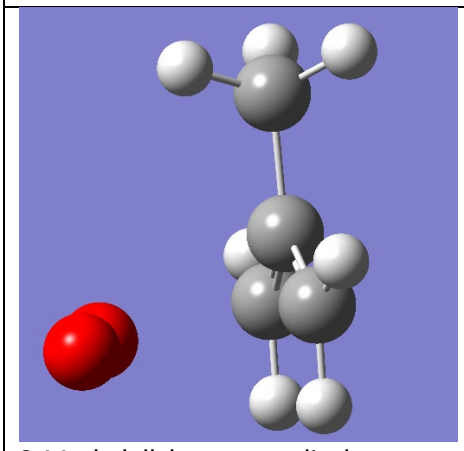
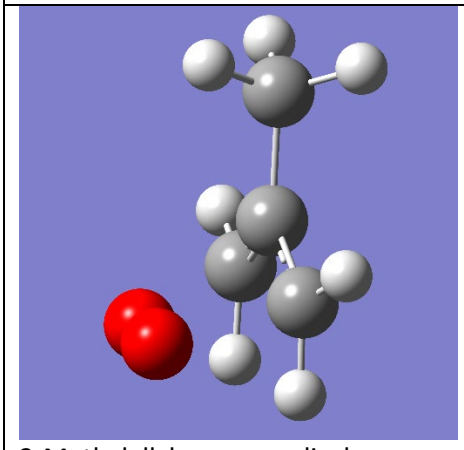
p /mbar	k^{2nd} (E-1MA) /10^{11} cm^3 mol^{-1} s^{-1}	k^{2nd} (Z-/E-1MA) /10^{11} cm^3 mol^{-1} s^{-1}	k^{2nd} (2MA) /10^{11} cm^3 mol^{-1} s^{-1}
1	3.6/4.1/3.6	3.3/3.7/3.4	4.0/4.5/5.2
2	4.1/4.4/3.9	4.0/4.3/3.7	3.8/4.8/5.1
3	4.2/4.4/4.6		3.7/4.9/5.1

Table S3: Calculated Stuctures of the different methylallyl peroxy radicals and their cationic ground states.

	Atom	Coordinates		
		X	Y	Z
 E-1-Methylallyl peroxy radical Neutral, S=2 CBS-QB3 (0 K): -306.434167	C	-0.774922	0.546856	0.291673
	H	1.208214	0.876339	1.238535
	H	-0.777322	1.374792	0.420212
	C	0.572825	0.067527	0.447255
	H	0.654641	0.871358	1.175200
	C	1.643493	0.319813	0.244338
	H	1.529914	1.121980	0.972773
	C	3.019853	-0.253473	0.103647
	H	3.049711	-1.056009	0.636095
	H	3.736888	0.518280	0.196857
	H	3.372694	0.653417	1.060331
	O	-1.693307	0.481432	0.234864
	O	2.947418	0.091646	0.157515
 E-1-methylallyl peroxy radical Cation, S=3 CBS-QB3 (0 K): -306.129399	C	-0.131652	1.274255	0.209313
	H	-0.820582	1.906209	-0.341011
	H	-0.330297	1.132357	1.267006
	C	0.954465	0.701707	-0.396709
	H	1.143926	0.856404	-1.453533
	C	1.827353	-0.083216	0.358741
	H	1.594878	-0.215633	1.415533
	C	3.025001	-0.740450	-0.142467
	H	3.218322	-0.580271	-1.201061
	H	3.887994	-0.417122	0.462599
	H	2.956879	-1.818241	0.080105
	O	-2.276504	-0.562382	0.116291
	O	-3.436261	-0.409803	-0.166654
 E-1-Methylallyl peroxy radical Cation, S=1 CBS-QB3 (0 K): -306.083828	C	-0.368093	1.078513	0.192169
	H	-1.109715	1.628164	-0.375861
	H	-0.478394	1.075375	1.271533
	C	0.758185	0.554462	-0.409235
	H	0.874317	0.608775	-1.486593
	C	1.759972	-0.010459	0.363841
	H	1.603841	-0.049463	1.441695
	C	3.022282	-0.549160	-0.140848
	H	3.858338	-0.028890	0.350990
	H	3.128735	-1.591874	0.195360
	H	3.128551	-0.489821	-1.222430
	O	-2.084215	-0.650285	0.157504
	O	-3.170753	-0.298766	-0.183786

 1-Methylallyl peroxy radical Neutral, S=2 CBS-QB3 (0 K): -306.435014	C	-2.109957	-0.691548	-0.223701
	H	-1.634454	-1.562746	-0.656089
	H	-3.192943	-0.657648	-0.238775
	C	-1.407206	0.301991	0.308843
	H	-1.918919	1.162074	0.734689
	C	0.088751	0.389464	0.391157
	H	0.415926	0.376812	1.435776
	C	0.669425	1.605072	-0.325035
	H	0.293139	2.523784	0.131679
	H	1.757206	1.595821	-0.244921
	H	0.383251	1.597600	-1.378928
	O	0.646534	-0.832358	-0.206874
	O	1.909806	-1.000838	0.120497
 1-Methylallyl peroxy radical Cation, S=3 CBS-QB3 (0 K): -306.130325	C	-2.525969	-1.394633	0.016763
	H	-1.752119	-2.126424	0.230574
	H	-3.536486	-1.769042	-0.114023
	C	-2.238357	-0.062784	-0.082720
	H	-3.019023	0.659350	-0.297101
	C	-0.918403	0.369087	0.095601
	H	-0.163184	-0.387816	0.306436
	C	-0.462448	1.745735	0.022350
	H	0.035632	1.998559	0.974207
	H	0.366573	1.804358	-0.701972
	H	-1.238426	2.471851	-0.209668
	O	2.318157	-0.214839	-0.063510
	O	3.454105	-0.609569	0.000959
 1-Methylallyl peroxy radical Cation, S=1 CBS-QB3 (0 K): -306.079903	C	-2.174441	-0.205063	0.158084
	H	-2.075929	-0.906282	0.982258
	H	-3.161917	-0.099586	-0.278533
	C	-1.134482	0.529839	-0.295049
	H	-1.240461	1.170393	-1.164683
	C	0.201018	0.490987	0.357984
	H	0.212666	0.103428	1.376156
	C	1.158755	1.610678	0.078270
	H	0.761819	2.500923	0.581080
	H	2.148269	1.406181	0.487955
	H	1.229115	1.831760	-0.988462
	O	0.735811	-0.778524	-0.484252
	O	0.991856	-1.792160	0.135314
 Z-1-Methylallyl peroxy radical Neutral, S=2 CBS-QB3 (0 K): -306.431463	C	2.390654	-0.862948	-0.061933
	H	3.194159	-0.896957	0.681971
	H	2.839325	-1.150403	1.018509
	H	1.653200	-1.620479	0.204879
	C	1.819199	0.520399	-0.154310
	H	2.526618	1.285787	-0.466795
	C	0.572380	0.921038	0.104211
	H	0.327933	1.972046	-0.020949
	C	-0.557964	0.064204	0.563081
	H	-1.023621	0.443406	1.475694
	H	-0.293445	-0.983386	0.702909
	O	-1.606941	0.106308	-0.474101
	O	-2.714282	-0.469580	-0.059086

 Z-1-Methylallyl peroxy radical Cation, S=3 CBS-QB3 (0 K): -306.124780	C	2.264221	-1.124215	0.235273
	H	2.243826	-1.953937	-0.489817
	H	1.594774	-1.338428	1.063857
	H	3.310104	-1.119053	0.580908
	C	2.016128	0.114769	-0.492737
	H	2.699376	0.312381	-1.318546
	C	1.023045	1.080265	-0.279872
	H	0.993579	1.933074	-0.948652
	C	0.108495	0.992240	0.734660
	H	-0.633113	1.770390	0.880251
	H	0.095990	0.172332	1.443280
	O	-2.087648	-0.521741	-0.151213
	O	-3.259335	-0.247647	-0.148189
 Z-1-Methylallyl peroxy radical Cation, S=1 CBS-QB3 (0 K): -306.080989	C	-1.932098	-0.856658	-0.540887
	H	-3.020405	-0.713989	-0.623441
	H	-1.823206	-1.920194	-0.288300
	H	-1.470369	-0.652090	-1.504107
	C	-1.455433	-0.043319	0.583257
	H	-1.916588	-0.268845	1.543791
	C	-0.524604	0.988854	0.584341
	H	-0.331016	1.495363	1.523474
	C	0.185132	1.371017	-0.533993
	H	0.878261	2.203756	-0.494630
	H	0.007737	0.939992	-1.512231
	O	2.043907	-0.172190	-0.308714
	O	1.710794	-1.058230	0.408606
 2-Methylallyl peroxy radical Neutral, S=4 CBS-QB3 (0K): -306.405230	C	-1.279898	-0.027991	0.000014
	C	-1.389677	-0.699053	1.209675
	H	-1.312565	-0.177905	2.156142
	H	-1.555871	-1.769456	1.240782
	C	-1.390038	-0.697519	-1.210463
	H	-1.556248	-1.767880	-1.242878
	H	-1.313210	-0.175172	-2.156292
	C	-1.006136	1.464453	0.000921
	H	-1.427589	1.947362	-0.883187
	H	-1.427295	1.946230	0.885786
	H	0.071665	1.655271	0.000862
	O	2.544791	0.473671	-0.000328
	O	2.319660	-0.710895	0.000066

 2-Methylallyl peroxy radical Neutral, S=2 CBS-QB3 (0K): -306.434067	C	2.169506	-0.822280	-0.000015
	H	2.160933	-1.475358	-0.880125
	H	3.106533	-0.264291	-0.000068
	H	2.161017	-1.475301	0.880145
	C	0.985630	0.110324	-0.000004
	C	1.098130	1.436634	0.000006
	H	0.232634	2.085719	0.000050
	H	2.074528	1.908062	0.000019
	C	-0.340074	-0.597843	0.000032
	H	-0.460958	-1.228206	-0.886912
	H	-0.460987	-1.228105	0.887044
	O	-1.434426	0.360949	-0.000036
	O	-2.602181	-0.246390	0.000002
 2-Methylallyl peroxy radical Cation, S=3 CBS-QB3 (0K): -306.114794	C	1.678889	1.366369	-0.127823
	H	1.754711	1.928497	0.804696
	H	2.638198	1.418075	-0.641642
	H	0.931227	1.859536	-0.755345
	C	1.268945	-0.059569	0.131766
	C	1.888944	-1.146866	-0.456454
	H	1.548585	-2.161008	-0.271276
	H	2.746763	-1.027370	-1.112444
	C	0.247528	-0.385619	1.019618
	H	-0.054376	-1.415472	1.179646
	H	-0.245480	0.372235	1.621389
	O	-1.944625	-0.144840	-0.454513
	O	-3.033557	0.192293	-0.073946
 2-Methylallyl peroxy radical Cation, S=1 CBS-QB3 (0K): -306.071162	C	1.581700	1.365121	-0.096527
	H	1.586236	1.924543	0.841327
	H	2.578521	1.418625	-0.532691
	H	0.890299	1.866479	-0.779914
	C	1.157432	-0.064363	0.127715
	C	1.858924	-1.142510	-0.349303
	H	1.516827	-2.159570	-0.188298
	H	2.793679	-1.018952	-0.887046
	C	0.023325	-0.370981	0.898549
	H	-0.262171	-1.401943	1.079107
	H	-0.475452	0.385923	1.495663
	O	-1.764010	-0.174743	-0.522839
	O	-2.780518	0.207404	-0.041005