Electronic Supplementary Information (ESI)

Endo-cyclization of unsaturated RO_2 radicals from the gas-phase ozonolysis of cyclohexadienes

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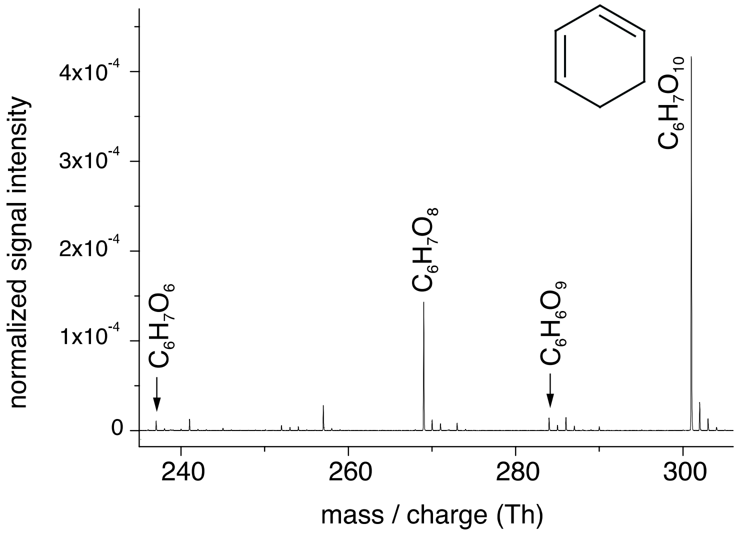


Fig. S1 Product mass spectrum recorded from the ozonolysis of 1,3-cyclohexadiene.

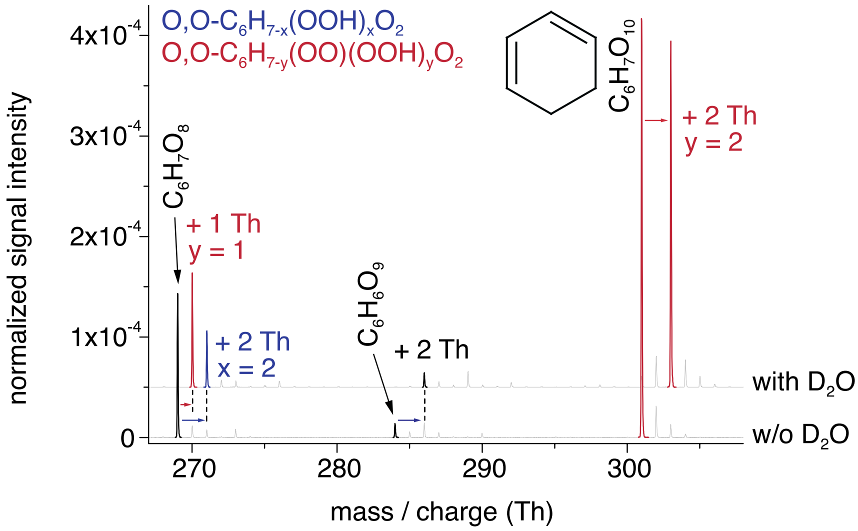


Fig. S2 Comparison of mass spectra from the ozonolysis of 1,3-cyclohexadiene recorded either in the absence (lower spectrum) or presence (upper spectrum) of heavy water used for H/D exchange of acidic H atoms.

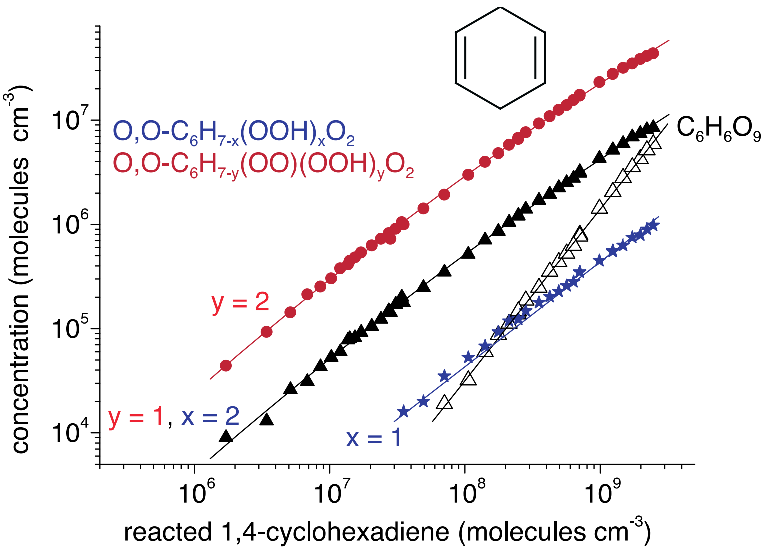


Fig. S3a Estimated RO_2 radical concentrations and the concentration of the closed-shell product $C_6H_6O_9$ as a function of converted 1,4-cyclohexadiene. The given concentrations were obtained using a calculated, lower end calibration factor for the ion-molecule reaction NO_3^- + HOM, see ref. S1. The black filled triangles represent the total RO_2 concentrations of $C_6H_7O_8$ consisting of the species O,O-$C_6H_{7-y}(OO)(OOH)_yO_2$ with y = 1 and O,O-$C_6H_{7-x}(OOH)_xO_2$ with x = 2. The red filled dots correspond to RO_2 radicals containing two hydroperoxide moieties and one endo-peroxide group. The blue stars correspond to RO_2 radicals containing one hydroperoxide moiety. The black open triangles correspond to the closed-shell product $C_6H_6O_9$. Initial reactant concentrations were $[O_3] = 6.4 \times 10^{11}$ and [1,4-cyclohexadiene] = $(7.0 - 10200) \times 10^9$ molecules cm^{-3}.

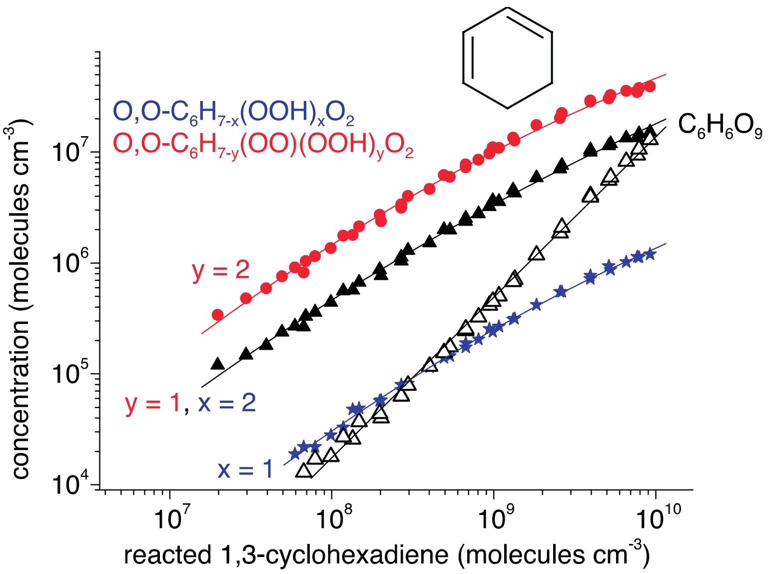


Fig. S3b Estimated RO_2 radical concentrations and the concentration of the closed-shell product $C_6H_6O_9$ as a function of converted 1,3-cyclohexadiene. The given concentrations were obtained using a calculated, lower end calibration factor for the ion-molecule reaction NO_3^- + HOM, see ref. S1. The black filled triangles represent the total RO_2 concentrations of $C_6H_7O_8$ consisting of the species O,O-$C_6H_{7-y}(OO)(OOH)_yO_2$ with y = 1 and O,O-$C_6H_{7-x}(OOH)_xO_2$ with x = 2. The red filled dots correspond to RO_2 radicals containing two hydroperoxide moieties and one endo-peroxide group. The blue stars correspond to RO_2 radicals containing one hydroperoxide moiety. The black open triangles correspond to the closed-shell product $C_6H_6O_9$. Initial reactant concentrations were $[O_3] = 6.4 \times 10^{11}$ and [1,3-cyclohexadiene] = $(2.1 - 970) \times 10^9$ molecules cm^{-3}.

Proposed reaction mechanisms of HOM formation from the ozonolysis of 1,4-cyclohexadiene (1,4-CHD)

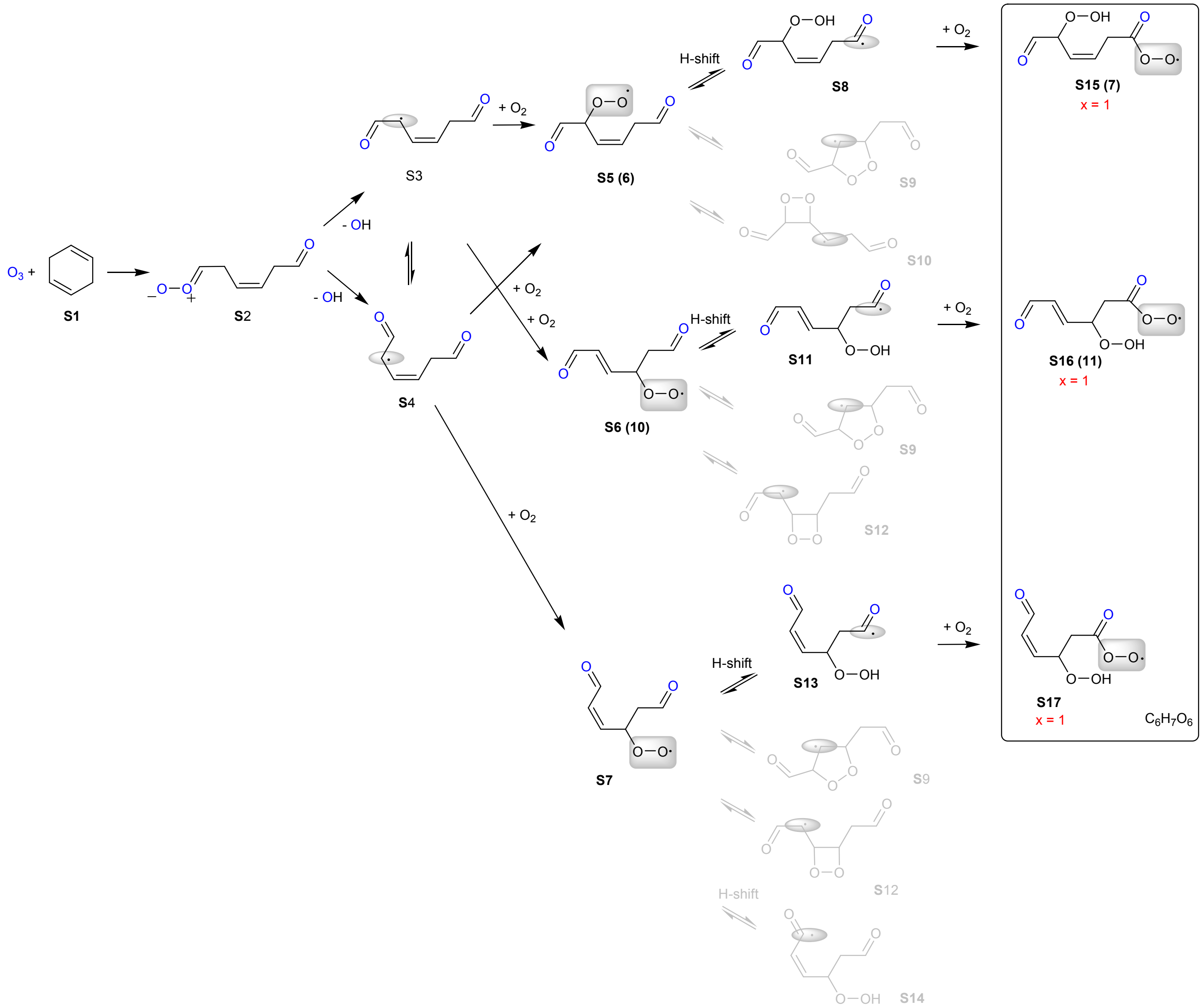
A proposed reaction mechanism describing the HOM formation of the ozone-initiated oxidation of 1,4-CHD is given in Schemes S1 – S4, which can be regarded as a representative for both cyclohexadienes. These schemes expand the simplified reaction mechanism as given in Schemes 2a and b in the main text. The species are successively numbered starting from S1. For the species already introduced in Schemes 2a and 2b in the main text, the corresponding numbering is added in brackets. The mechanism stated here is based on mechanistic information already given in the literature.[S1-S5]

In Scheme S1, ozone attacks one of the two identical double bonds of 1,4-CHD **S1** forming the Criegee intermediate **S2**. Species **S2** can be rearranged under OH radical release giving the alkyl radical **S3** and its allylic isomer **S4**. Oxygen molecules can add rapidly forming the first RO_2 radicals **S5** (**6**), **S6** (**10**), and **S7** respectively. These RO_2 radicals might react via an intramolecular H atom transfer with subsequent addition of an oxygen molecule (**S5** $\rightarrow$ **S8** $\rightarrow$ **S15**, **S6** $\rightarrow$ **S11** $\rightarrow$ **S16**, and **S7** $\rightarrow$ **S13** $\rightarrow$ **S17**) forming the RO_2 radicals **S15** (**7**), **S16** (**11**), and **S17,** which contain a first hydroperoxide group each. The possible attack of the RO_2 radical functional groups in **S5**, **S6** and **S7** at the second, still intact double bond (**S5** $\rightarrow$ **S9**, **S5** $\rightarrow$ **S10, S6** $\rightarrow$ **S9, S6** $\rightarrow$ **S12, S7** $\rightarrow$ **S9** and **S7** $\rightarrow$ **S12**) was calculated to be negligible. Thus, these reaction pathways were not further pursued and are shown in grey.

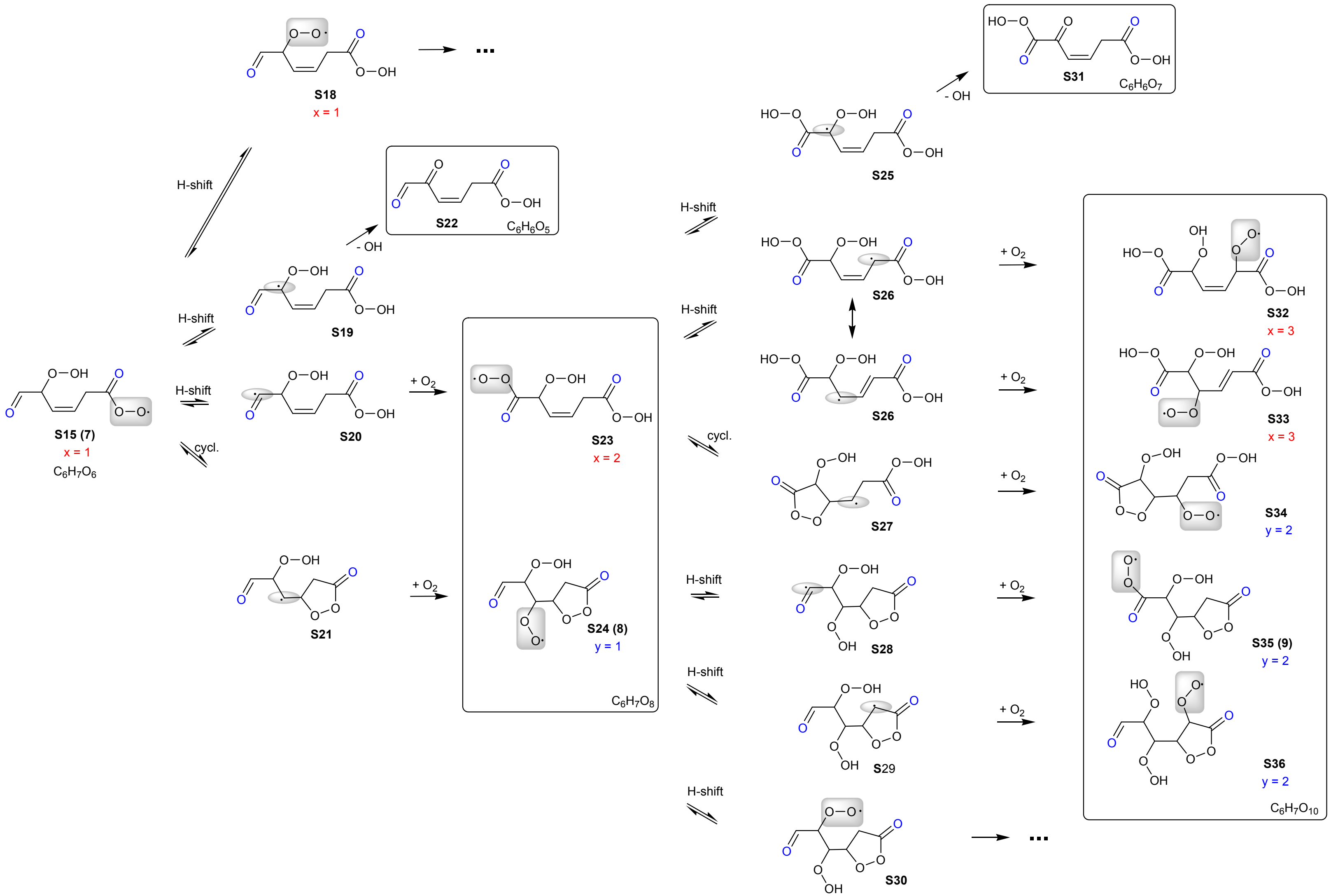
Scheme S2 shows possible reaction pathways of the RO_2 radical **S15**. Species **S15** can react via an intramolecular H atom scrambling between the peroxy radical group and the hydroperoxide group (**S15** $\rightarrow$ **S18**). Reaction product **S18** can undergo further reactions, but those pathways are not shown here. Otherwise, an H atom transfer with subsequent OH elimination can take place for **S15** forming the closed-shell product **S22** (**S15** $\rightarrow$ **S19** $\rightarrow$ **S22**). Furthermore, species **S15** can react via the well-established intramolecular H atom transfer with subsequent O_2 addition (**S15** $\rightarrow$ **S20** $\rightarrow$ **S23**) forming the next RO_2 radical **S23**. As shown in Scheme 2a in the main text, the RO_2 radical functional group can also internally attack the double bond of **S15**. This attack forms an endoperoxide group containing alkyl radical to which O_2 can rapidly add (**S15** $\rightarrow$ **S21** $\rightarrow$ **S24**) giving species **S24** (**8**).

All these competing reaction pathways can further take place starting from the intermediate reaction products **S23** and **S24** forming the higher oxidized reaction products **S31** – **S36**.

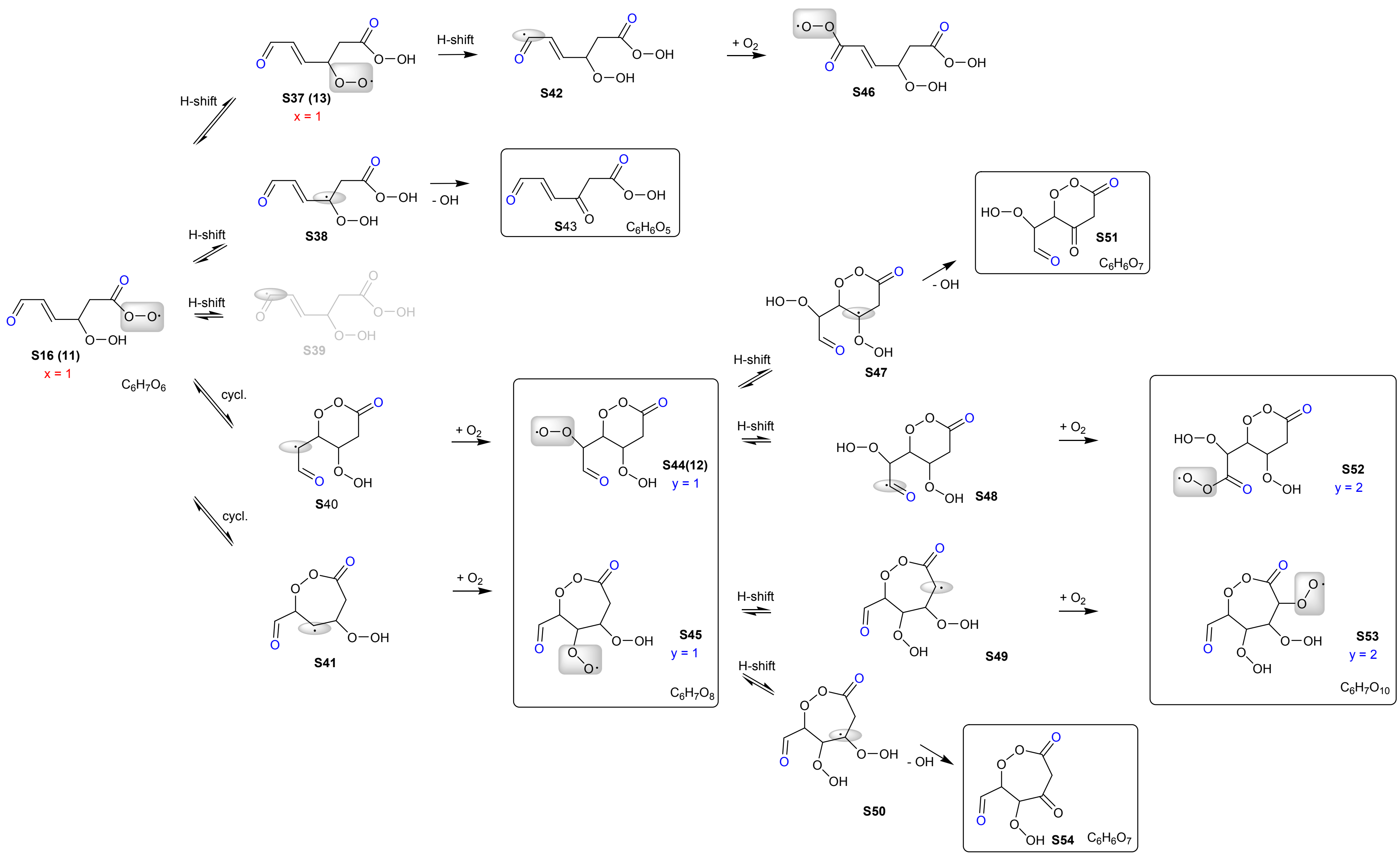
Reaction Schemes S3 and S4 show the reaction pathways starting from species **S16** (**11**) and **S17**. These reaction products react via the same reaction pathways as shown for species **S15** leading to the reaction products **S37** – **S65**. The relevant reaction products of **S16** are also shown in Scheme 2b in the main text.



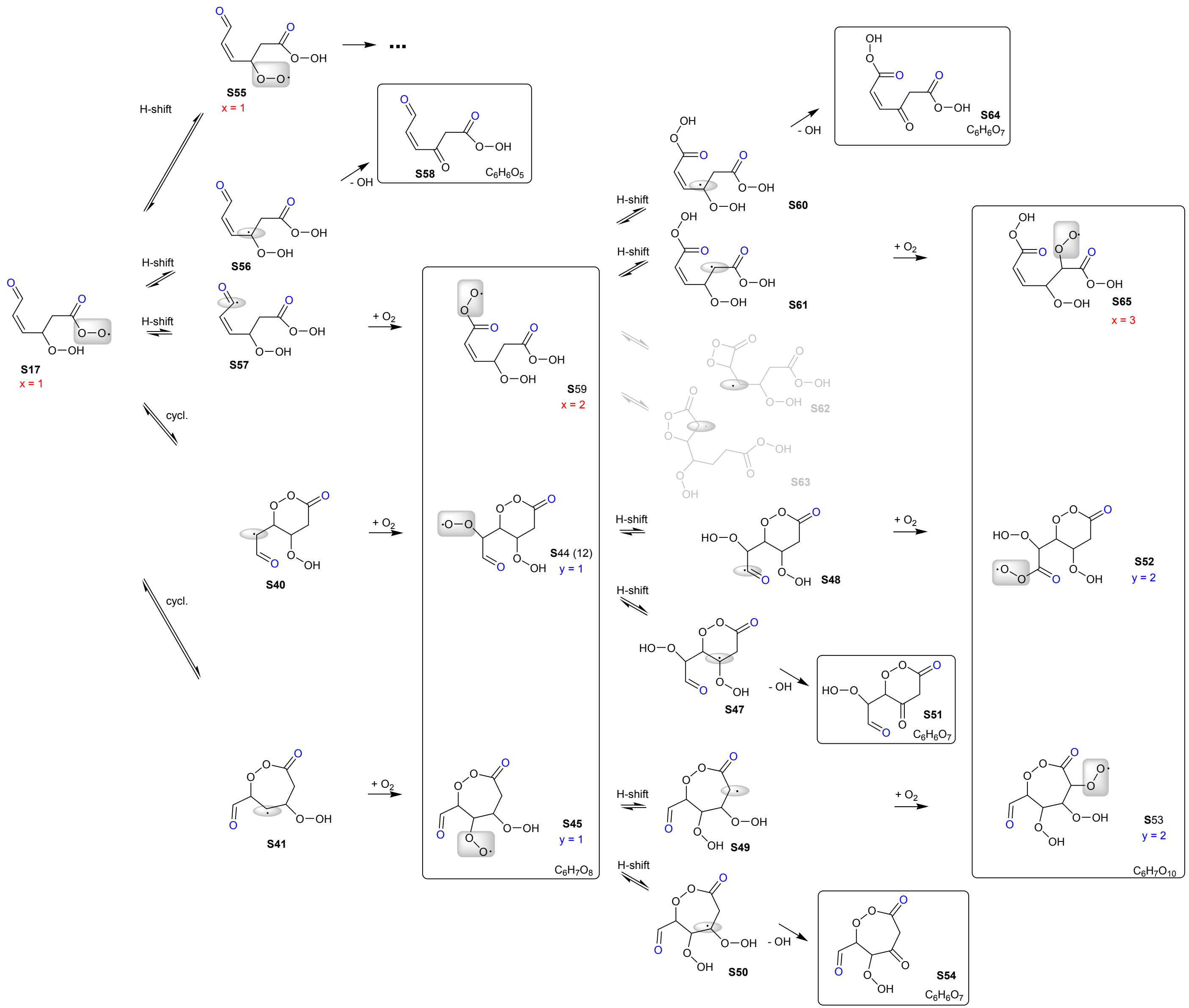
*Scheme S1 First reaction steps of the ozonolysis of 1,4-CHD. Oxygen atoms arising from the attacking ozone are highlighted in blue, alkyl radical functional groups with a shaded oval and RO_2 radical functional groups with a shaded rectangle. Detected species are surrounded by a solid rectangle. Species in grey (**S9**, **S10**, **S12** and **S14**) are not significantly formed according to the calculations. The numbering in brackets belongs to the numbering in the main text.*



*Scheme S2 Further reaction steps of RO_2 radical **S15 (7)**. The numbering in brackets belongs to the numbering in the main text.*



*Scheme S3 Further reaction steps of RO_2 radical **S16** (**11**). The numbering in brackets belongs to the numbering in the main text. The species in grey (**S39**) is not significantly formed according to the calculations.*



*Scheme S4. Further reaction steps of RO_2 radical **S16.** The numbering in brackets belongs to the numbering in the main text. Species in grey (**S61** and **S62**) are probably not significantly formed according to calculations of the analogous reaction channels (**S5** $\rightarrow$ **S9**, **S5** $\rightarrow$ **S10**)*

Quantum-chemical and rate coefficient calculations – Methodology

Rate calculations for the unimolecular reactions of the following species were carried out: the first-generation peroxy radicals **S5**, **S6** and **S7** ($C_6H_7O_4$), the second-generation peroxy radicals **S15**, **S16** and **S17** ($C_6H_7O_6$), as well as **S24** (**8**) ($C_6H_7O_8$), one of the third-generation radicals formed after endo-cyclisation of **S15** and O_2 addition.

Geometries and harmonic vibrational frequencies of all minima and transition states were obtained at the M06-2X[S6]/TZVP[S7] level of theory. The unrestricted Kohn-Sham (UKS) formalism was chosen for the radicals. These density functional calculations were carried out with the Gaussian 09 program package.[S8] Single-point energy calculations using the explicitly correlated CCSD(F12*)(T) method[S9-10] with the def2-TZVPP basis set[S11] were then performed on these structures. To this end, the Turbomole 7.0 package[S12] was used. Restricted open-shell Hartree-Fock (ROHF) determinants served as references for the coupled-cluster calculations in all cases. For the explicitly correlated terms, ansatz 2 in combination with model B was utilized (see Ref. [S13] for details). The F12 amplitudes were obtained with the rational generator approach according to Ref. [S14]. A Slater-type germinal correlation factor with exponent 1.0 a_0^{-1}, represented by a linear combination of six Gaussians, was selected. The perturbative triples correction was scaled by the ratio of MP2-F12 and MP2 correlation energies.[S15]

All rate coefficients given in this work are high-pressure limits obtained with conventional transition state theory in the rigid rotor—harmonic oscillator approximation, at a fixed temperature of 300 K. Thermal tunneling correction factors were included, calculated[S16] from semi-classical one-dimensional transmission factors based on the procedure by Garrett and Truhlar.[S17] Potential energy curves along the intrinsic reaction coordinate were calculated at the M06-2X/TZVP level. The effect of hindered internal rotations was not explicitly accounted for in this work. It has to be emphasized that due to this limitation, the rate coefficients are probably overestimated, because all relevant isomerization steps involve a cyclic transition state formed from an open-chain reactant. Furthermore, excess energy from the O_2 additions could lead to chemically activated intermediates, an effect which is not reflected by the canonical rate coefficients reported here.

Supplementary References:

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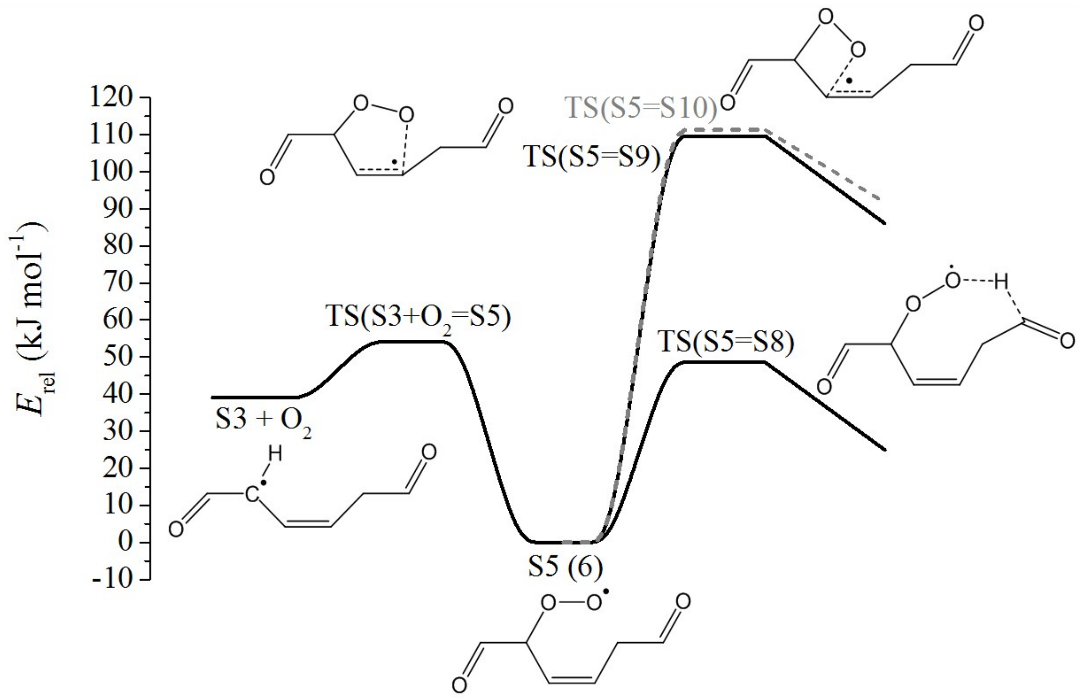
Potential Energy Surfaces and TST Rate Coefficients

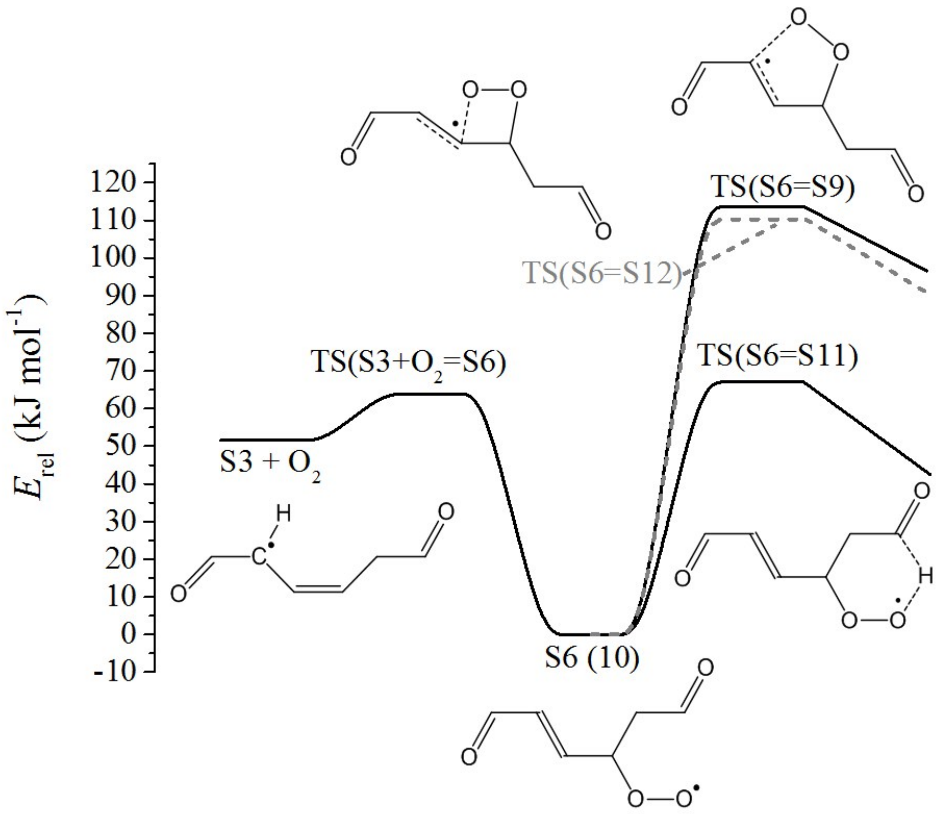
All reported energies were obtained at the CCSD(F12*)(T)/def2-TZVPP//M06-2X/TZVP level, including zero-point vibrational corrections. In the tables below, the potential energy diagrams, the isomerization barriers and room-temperature rate coefficients are given. Note: For each species, all conceivable H shifts were considered. However, some of these channels exhibited very high barriers, rendering them kinetically insignificant. Thus, they were excluded from the potential energy diagrams and rate coefficient tables.

Isomerization and Dissociation Reactions of S5 (1st Generation Peroxy Radical from 2-Addition to S3/S4)



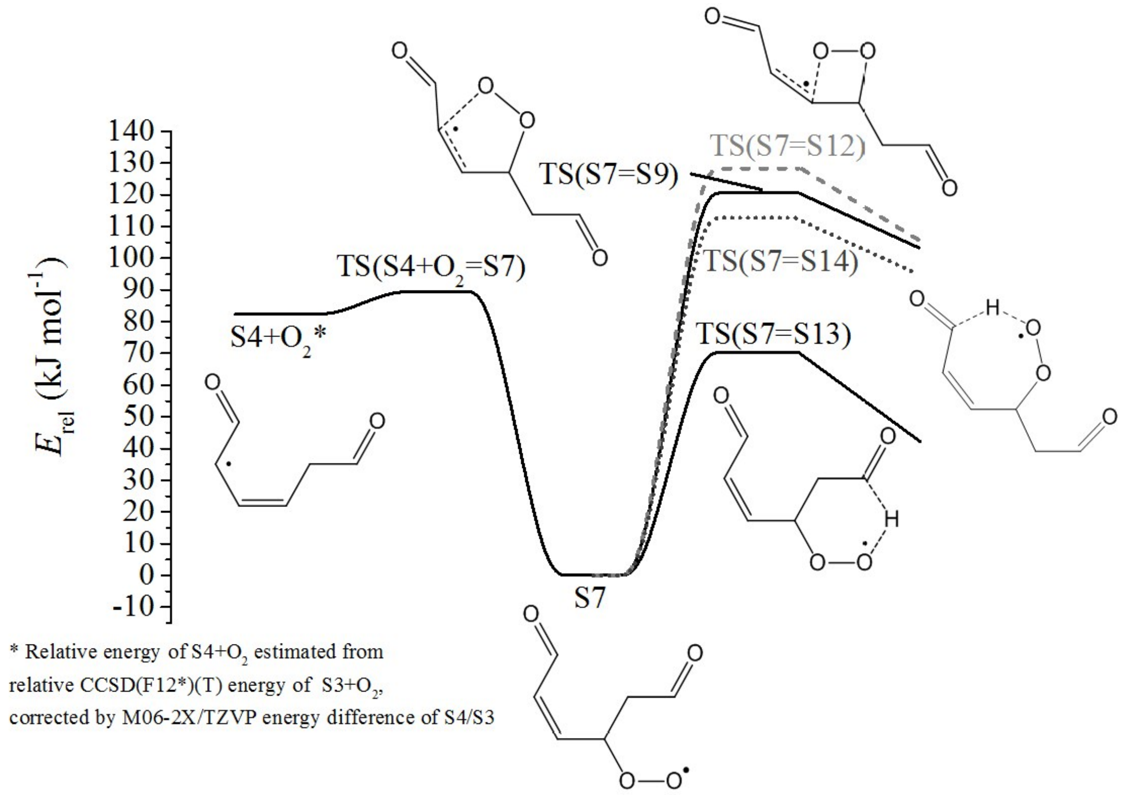
Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S5 → S3+O_2	54.2	6.6×10^{2}
S5 → S8	48.7	4.7×10^{3}
S5 → S9	109.7	4.7×10^{-8}
S5 → S10	111.4	1.1×10^{-7}

Isomerization and Dissociation Reactions of S6 (1st Generation Trans Peroxy Radical from 4-Addition to S3)



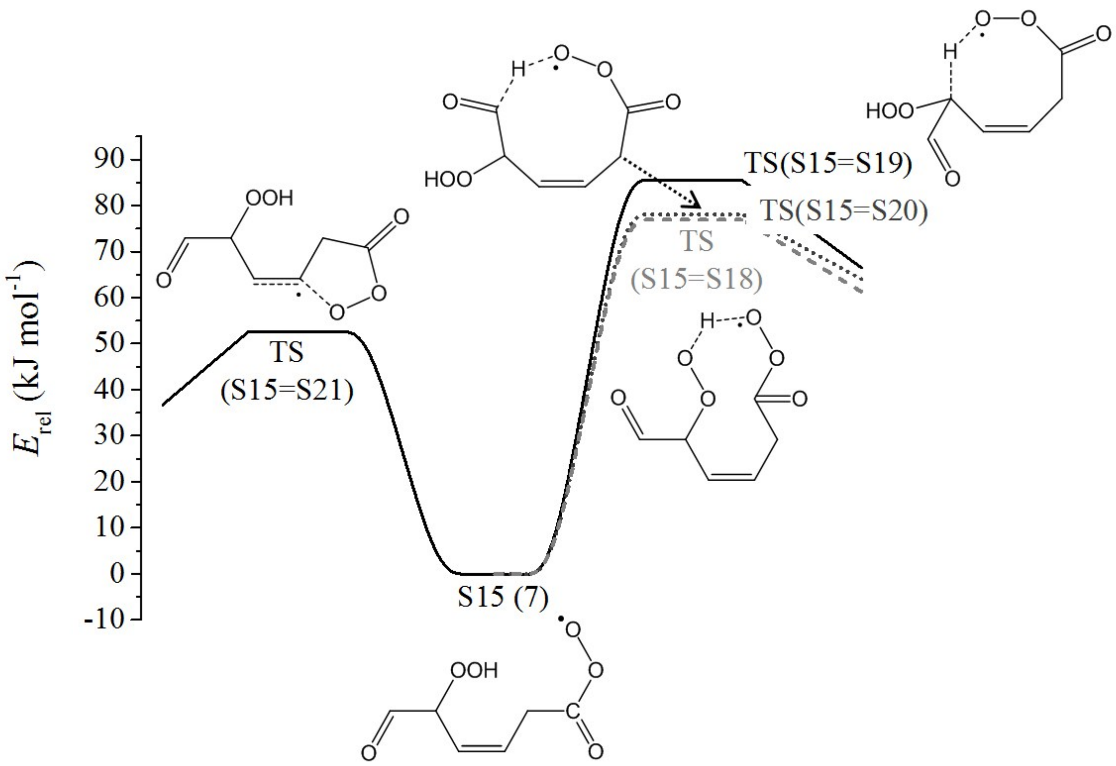
Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S6 → S3+O_2	63.9	4.0×10^{1}
S6 → S9	113.6	1.1×10^{-8}
S6 → S11	67.0	3.7×10^{1}
S6 → S12	110.3	1.1×10^{-7}

Isomerization and Dissociation Reactions of S7 (1st Generation Cis Peroxy Radical from 4-Addition to S4)



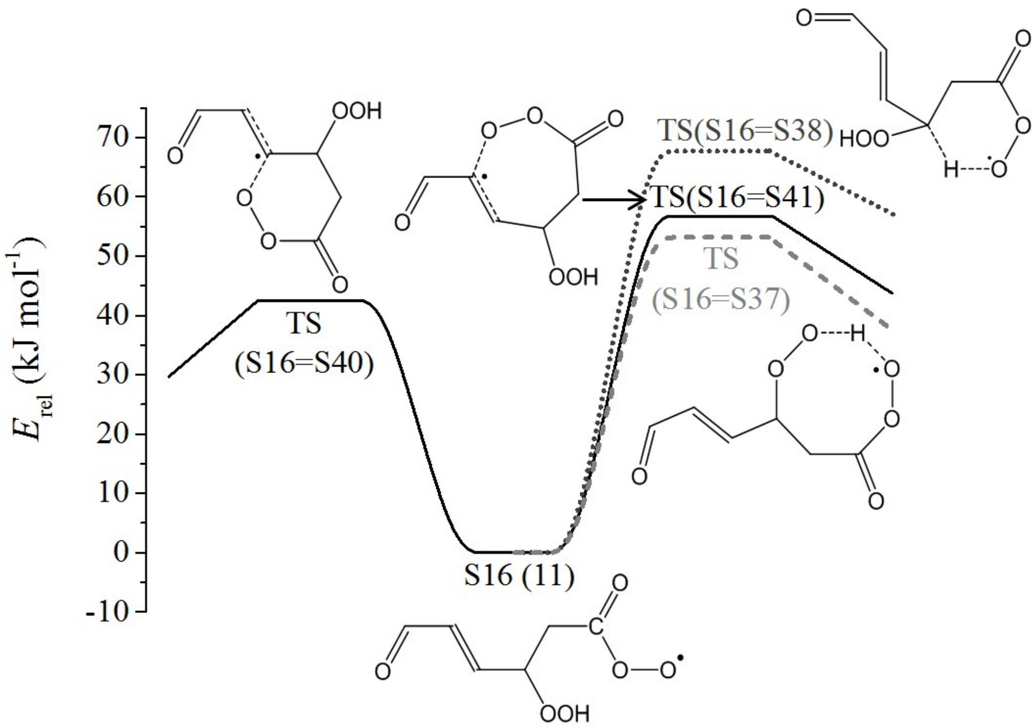
Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S7 → S4 + O_2	89.5	4.2×10^{-3}
S7 → S9	120.5	1.1×10^{-9}
S7 → S12	128.3	1.6×10^{-10}
S7 → S13	70.3	1.1×10^{1}
S7 → S14	112.7	1.4×10^{-5}

Isomerization Reactions of S15 (2nd Generation Peroxy Radical)



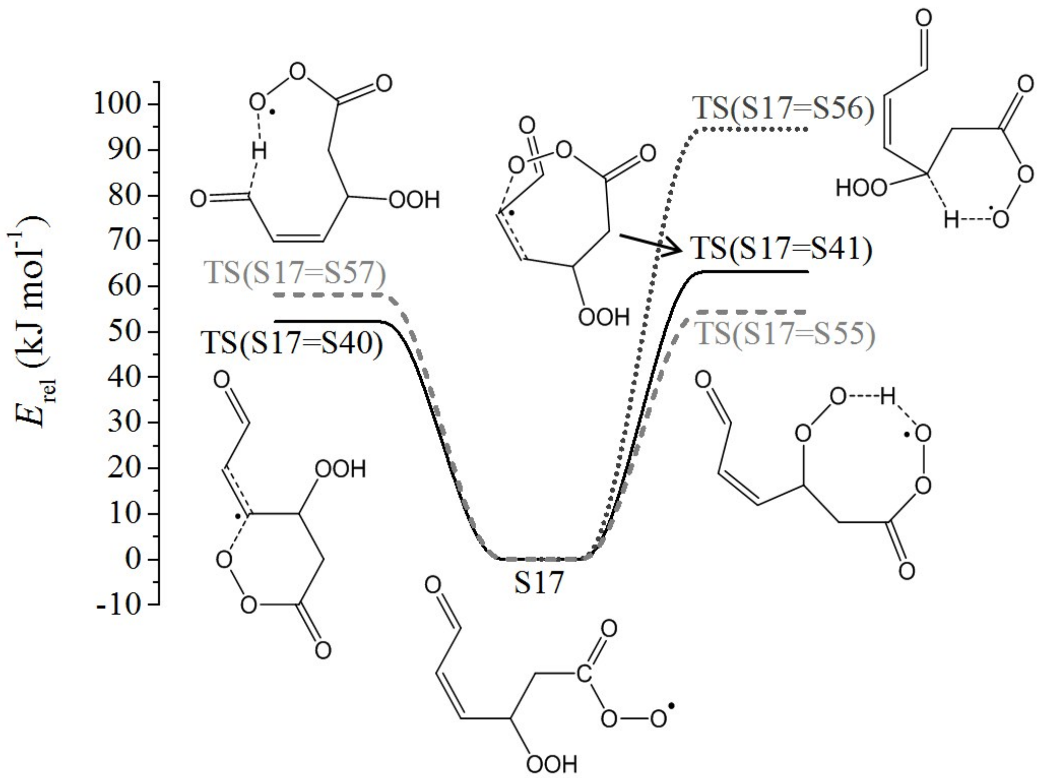
Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S15 → S18	76.9	2.3
S15 → S19	85.6	5.0×10^{-3}
S15 → S20	78.1	4.7×10^{-1}
S15 → S21	52.6	1.4×10^{3}

Isomerization Reactions of S16 (2nd Generation Peroxy Radical)



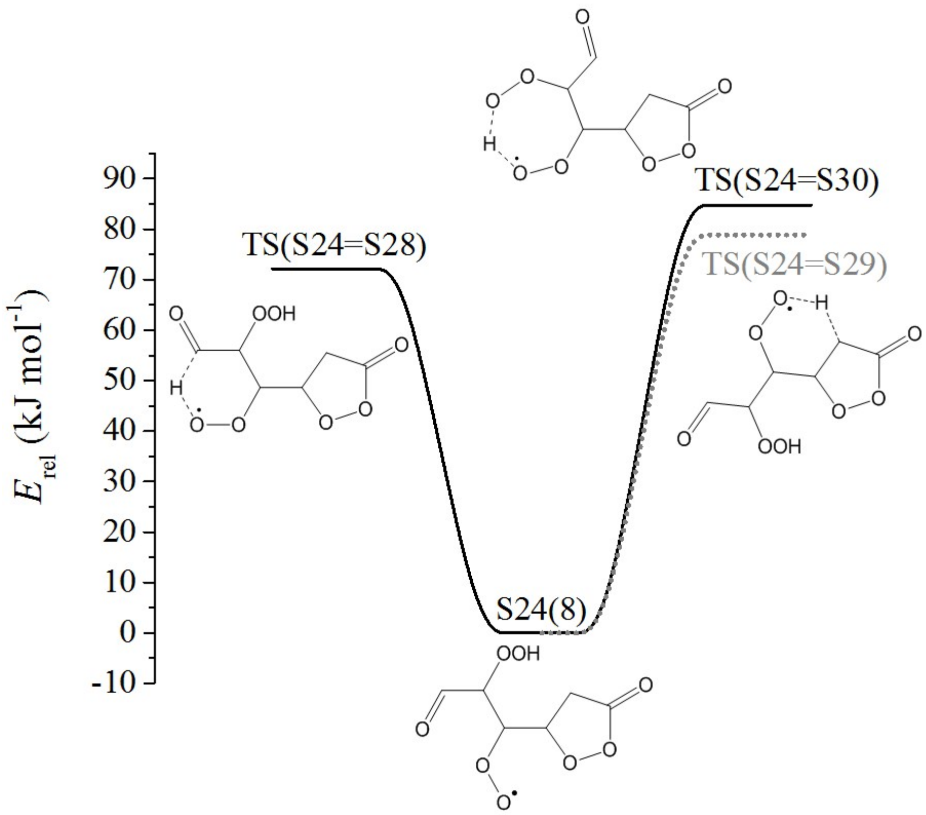
Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S16 → S37	53.2	1.7×10^4
S16 → S38	67.7	1.1×10^2
S16 → S40	42.6	7.0×10^4
S16 → S41	56.8	7.2×10^1

Isomerization Reactions of S17 (2nd Generation Peroxy Radical)



Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S17 → S40	52.2	1.2×10^{3}
S17 → S41	63.2	3.8
S17 → S55	54.4	1.1×10^{4}
S17 → S56	94.6	2.1×10^{-3}
S17 → S57	58.2	5.6×10^{2}

Isomerization Reactions of S24 (3rd Generation Peroxy Radical after Cyclization)



Reaction	E_0[CCSD(T)]/kJ mol^{-1}	$k_{TST,tun}$(295K) / s^{-1}
S24 → S28	72.1	5.9
S24 → S29	78.9	5.2×10^{-1}
S24 → S30	84.8	5.3

Cartesian Coordinates (in Å) of Stable Species and Transition States at the M06-2X/TZVP Level of Theory

S5

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C    1.601211    1.287966   -0.204605
H    2.675647    1.453417   -0.399552
C    1.102090   -0.143392   -0.427833
H    0.466142   -0.142454   -1.316012
C    0.391136   -0.695746    0.770954
H    1.006432   -1.308753    1.419409
C   -0.869889   -0.432937    1.081969
H   -1.264756   -0.869691    1.995164
C   -1.821522    0.425591    0.303337
H   -1.417177    0.774774   -0.645337
H   -2.053903    1.317155    0.898964
C   -3.123054   -0.300623    0.052403
H   -3.583106   -0.774556    0.942654
O    0.863509    2.163098    0.135680
O   -3.651758   -0.378923   -1.020079
O    2.220321   -0.975535   -0.796694
O    3.129288   -0.970519    0.137012
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S6

```
C -3.189241   -0.762148   -0.341240
H -3.630755   -1.576220   -0.942180
C -1.711689   -0.813286   -0.168706
H -1.197562   -1.679677   -0.568917
C -1.072563    0.183380    0.430922
H -1.651383    1.033264    0.784372
C  0.399918    0.248306    0.689095
H  0.575740    0.229491    1.769352
C  1.246281   -0.798973   -0.006108
H  1.119461   -0.753041   -1.087813
H  0.932551   -1.789772    0.338348
C  2.715318   -0.656984    0.329696
H  2.945896   -0.283764    1.347610
O -3.886122    0.098428    0.126946
O  3.594632   -0.946688   -0.428243
O  0.885564    1.579143    0.332501
O  0.728164    1.821361   -0.936545
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S7

```
C -2.762961   -0.744682    0.042671
H -3.844908   -0.958430    0.010522
C -2.352537    0.571410   -0.485692
H -3.116046    1.150756   -0.991045
C -1.126445    1.076198   -0.343550
H -0.897902    2.054240   -0.755664
C  0.024197    0.401742    0.334712
H -0.293384   -0.123681    1.235542
C  0.778515   -0.545358   -0.589515
H  1.192142   -0.014446   -1.446474
H  0.067752   -1.299223   -0.939284
C  1.884296   -1.271772    0.141940
H  1.646590   -1.582315    1.178893
O -1.996307   -1.563468    0.493425
O  2.945272   -1.531217   -0.348202
O  0.942239    1.416519    0.845447
O  1.430718    2.159149   -0.102655
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S15

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C -3.028188    0.208433   -0.560258
H -3.235213    1.197512   -1.004316
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C	-1.559376	-0.199881	-0.592391
H	-1.396399	-0.697579	-1.558148
C	-1.190478	-1.107296	0.550984
H	-2.006319	-1.426584	1.188620
C	0.051423	-1.493934	0.806012
H	0.242506	-2.109287	1.677650
C	1.246274	-1.147663	-0.035588
H	0.989751	-1.011861	-1.089218
H	1.994365	-1.941241	-0.007332
C	1.895914	0.129663	0.422629
H	-0.335399	1.574234	1.047813
O	-3.889257	-0.493231	-0.115920
O	1.533945	0.889774	1.256536
O	-0.751089	0.961647	-0.680709
O	-1.076182	1.769001	0.447860
O	3.110071	0.482125	-0.223066
O	3.479175	-0.349458	-1.160125

S16

C	3.269812	0.162034	-0.098436
H	3.829883	1.097201	0.077321
C	1.875396	0.140907	0.422470
H	1.550153	1.013210	0.977572
C	1.092948	-0.908433	0.195942
H	1.494200	-1.742314	-0.374910
C	-0.312968	-1.097532	0.682167
H	-0.297937	-1.707054	1.594069
C	-1.079225	0.195627	1.017049
H	-0.500370	0.815035	1.693460
H	-2.012378	-0.086282	1.503830
C	-1.477323	0.925483	-0.231210
H	-2.755908	-1.517748	-0.530983
O	3.783275	-0.757696	-0.678243
O	-2.252565	0.554001	-1.046036
O	-0.934151	-1.837433	-0.353327
O	-2.265713	-2.129342	0.042967
O	-0.888147	2.194784	-0.509805
O	-0.132635	2.678116	0.435913

S17

C	-3.017334	-0.096488	-0.218995
H	-4.093549	0.126072	-0.118984
C	-2.220124	0.028260	1.017430
H	-2.723053	0.455028	1.876913
C	-0.953662	-0.371732	1.128730
H	-0.443814	-0.256461	2.081561
C	-0.115898	-0.992859	0.050415
H	-0.684018	-1.730163	-0.519402
C	0.437678	0.037888	-0.962613
H	-0.376935	0.639952	-1.348747
H	0.916720	-0.508505	-1.772444
C	1.514407	0.852197	-0.317227
H	2.534146	-1.675804	-0.197356
O	-2.562640	-0.420746	-1.290422
O	2.653477	0.549294	-0.186148
O	0.936252	-1.625055	0.766978
O	1.777219	-2.284066	-0.167222
O	1.157355	2.100028	0.268830
O	-0.086650	2.456330	0.084487

S24

C	-2.313289	1.256456	0.100401
H	-2.781361	1.176661	1.094166
C	-0.842857	0.833776	0.027819
H	-0.332710	1.666501	-0.468494

C	-0.633298	-0.392798	-0.856648
C	0.797182	-0.903147	-0.986103
H	0.776739	-1.782826	-1.629304
C	1.807427	0.132538	-1.429687
H	1.383828	1.025843	-1.882872
H	2.548523	-0.282852	-2.112457
C	2.518983	0.492291	-0.142760
H	-0.103481	-0.992496	1.877808
O	-2.869126	1.704786	-0.860309
O	3.247311	1.398405	0.087698
O	-0.229248	0.780824	1.288744
O	-0.780493	-0.308352	2.017626
O	2.225257	-0.439297	0.806060
O	1.304607	-1.393939	0.274900
H	-1.012246	-0.137061	-1.852080
O	-1.362221	-1.569607	-0.417938
O	-2.596610	-1.321378	-0.109894

TS(S5 → S3+O_2)

C	2.436809	0.374736	-0.219852
H	2.915611	0.892465	0.632766
C	0.963070	0.408615	-0.234946
H	0.490632	0.007880	-1.126009
C	0.275151	1.323907	0.606490
H	0.844229	1.781097	1.410538
C	-1.053896	1.543091	0.553402
H	-1.498848	2.174563	1.313669
C	-1.961519	1.025627	-0.529961
H	-1.524797	1.182888	-1.517464
H	-2.918403	1.549301	-0.484153
C	-2.228965	-0.463330	-0.386068
H	-2.806009	-0.768960	0.503821
O	3.094208	-0.195186	-1.051268
O	-1.835015	-1.273351	-1.176910
O	0.734225	-1.278600	0.790991
O	-0.254207	-1.264753	1.503743

TS(S5 → S8)

C	-2.433678	-0.413844	-0.195325
H	-2.594762	-1.501960	-0.102116
C	-1.266726	0.123960	0.634350
H	-1.699422	0.463581	1.585444
C	-0.596046	1.284206	-0.045613
H	-1.293791	1.918123	-0.582838
C	0.691563	1.605069	-0.042685
H	0.989929	2.480567	-0.607999
C	1.816928	0.845290	0.611643
H	1.520230	0.446621	1.582223
H	2.709852	1.459335	0.720791
C	2.171454	-0.343413	-0.274934
H	1.164345	-1.091170	-0.364623
O	-3.138592	0.288385	-0.859030
O	3.191405	-0.569767	-0.819330
O	-0.423320	-0.949935	1.012021
O	-0.016662	-1.616520	-0.128098

TS(S5 → S9)

C	2.774156	0.337189	-0.033359
H	2.947657	1.395143	-0.299890
C	1.430671	0.073114	0.651553
H	1.614652	-0.040037	1.726118
C	0.748705	-1.087844	-0.022672
H	1.377453	-1.802431	-0.538203
C	-0.572774	-0.902260	-0.366877
H	-0.909639	-1.451846	-1.243582

C	-1.681562	-0.459131	0.549959
H	-1.298800	0.230284	1.304409
H	-2.094820	-1.334815	1.056678
C	-2.811656	0.221946	-0.194966
H	-2.504082	0.996657	-0.918155
O	3.570255	-0.529028	-0.245253
O	-3.967283	-0.042549	-0.011692
O	0.565172	1.179332	0.479835
O	0.024647	1.005865	-0.796540

TS(S5 → S10)

C	-2.730835	-0.428762	-0.475731
H	-3.386093	0.274744	-1.020536
C	-1.245454	-0.108481	-0.552971
H	-0.797583	-0.682349	-1.371741
C	-0.566347	-0.258197	0.796788
H	-1.170354	-0.618893	1.619454
C	0.802268	-0.242302	0.922779
H	1.222768	-0.372849	1.914618
C	1.727768	0.098854	-0.193634
H	1.616256	1.172091	-0.413765
H	1.490982	-0.431142	-1.119007
C	3.177237	-0.143081	0.152698
H	3.477458	0.155390	1.177236
O	-3.154265	-1.373293	0.125525
O	3.976008	-0.609050	-0.607514
O	-1.031678	1.274242	-0.750506
O	-0.970222	1.582453	0.646765

TS(S6 → S3+O_2)

C	-3.052197	-0.564197	-0.562107
H	-3.478828	-0.700062	-1.570600
C	-1.578073	-0.548241	-0.482325
H	-1.030196	-0.709071	-1.402991
C	-0.951671	-0.342007	0.700004
H	-1.568243	-0.177898	1.577817
C	0.450948	-0.199063	0.822242
H	0.859849	-0.075086	1.818389
C	1.384453	-0.642742	-0.255448
H	1.142161	-0.107061	-1.184458
H	1.275102	-1.709235	-0.470306
C	2.832049	-0.354881	0.070725
H	3.020352	0.587191	0.622297
O	-3.775703	-0.440504	0.395504
O	3.736866	-1.074051	-0.243220
O	0.567449	1.819696	0.408599
O	0.129732	2.044611	-0.704469

TS(S6 → S9)

C	3.079569	-0.032076	0.488734
H	3.646236	0.628237	1.165016
C	1.589998	0.065090	0.572053
H	1.186223	0.542214	1.457228
C	0.812953	-0.778941	-0.201372
H	1.261564	-1.551174	-0.812532
C	-0.539910	-0.210768	-0.525263
H	-0.648963	-0.208752	-1.617902
C	-1.737576	-0.869083	0.133616
H	-1.633266	-0.885683	1.218776
H	-1.810015	-1.902224	-0.222318
C	-3.029157	-0.169465	-0.232691
H	-3.077090	0.239565	-1.261424
O	3.641534	-0.765210	-0.279400
O	-3.960426	-0.069050	0.512069
O	-0.479887	1.138336	-0.057421
O	0.801287	1.584583	-0.342411

TS(S6 → S11)

C	-3.391421	-0.670016	-0.130076
H	-3.910643	-1.626112	-0.319533
C	-1.916256	-0.759821	0.039436
H	-1.479640	-1.752438	0.020786
C	-1.186708	0.338997	0.198808
H	-1.685348	1.304804	0.200310
C	0.290954	0.382868	0.418521
H	0.487651	0.665358	1.459549
C	1.040452	-0.901413	0.070569
H	0.698096	-1.275128	-0.898394
H	0.911424	-1.683708	0.820035
C	2.529918	-0.631596	-0.077665
H	2.668887	0.642434	-0.130657
O	-4.009939	0.359512	-0.074461
O	3.415771	-1.407952	-0.101192
O	0.800170	1.427262	-0.411134
O	2.057491	1.767512	0.053080

TS(S6 → S12)

C	-2.940586	-0.830969	-0.464370
H	-3.360835	-1.332201	-1.351877
C	-1.501472	-0.547647	-0.504590
H	-0.944521	-0.812311	-1.395213
C	-0.908456	0.147251	0.525775
H	-1.509155	0.332485	1.408841
C	0.593302	0.395688	0.585619
H	0.860174	0.847898	1.546831
C	1.509795	-0.760328	0.260600
H	1.288496	-1.196530	-0.712957
H	1.366112	-1.531761	1.026231
C	2.967086	-0.353847	0.297268
H	3.248285	0.351571	1.104575
O	-3.647328	-0.551229	0.476446
O	3.788444	-0.766123	-0.469433
O	0.641776	1.389918	-0.439368
O	-0.691214	1.807430	-0.296177

TS(S7 → S4 + O_2)

C	-1.995949	-0.971979	-0.333507
H	-1.092082	-1.215098	-0.907169
C	-1.867860	-0.168825	0.892183
H	-2.820284	-0.018660	1.390000
C	-0.760129	0.388490	1.447292
H	-0.924336	0.978313	2.343068
C	0.563581	0.433606	0.943833
H	1.267091	0.999519	1.545622
C	1.168980	-0.547126	-0.008713
H	0.759238	-0.402684	-1.016626
H	0.950040	-1.579825	0.275264
C	2.667807	-0.372200	-0.119995
H	3.027488	0.675722	-0.079600
O	-3.073854	-1.368633	-0.708564
O	3.434028	-1.280946	-0.256337
O	0.283571	1.970647	-0.418659
O	-0.621962	1.677797	-1.176080

TS(S7 → S9)

C	2.228490	0.916088	-0.088433
H	3.174433	1.000501	-0.646234
C	2.036745	-0.388108	0.618405
H	2.959623	-0.858917	0.946069
C	0.851019	-0.800962	1.189422
H	0.835942	-1.468056	2.040555
C	-0.364294	-0.734119	0.300171

H	-0.817181	-1.733288	0.302626
C	-1.397107	0.335088	0.638695
H	-0.895486	1.304236	0.577726
H	-1.787240	0.178295	1.644638
C	-2.548688	0.304617	-0.338758
H	-2.278705	0.434038	-1.402229
O	1.437235	1.817036	-0.040633
O	-3.691489	0.148917	-0.006771
O	0.143663	-0.453769	-1.006922
O	1.357044	-1.093739	-1.118194

TS(S7 → S12)

C	1.816068	1.085703	-0.278908
H	0.976133	1.072569	-0.991126
C	1.902428	-0.025447	0.679458
H	2.862144	-0.131993	1.172020
C	0.934360	-0.991503	0.874870
H	1.146681	-1.756967	1.611659
C	-0.511748	-0.893909	0.399221
H	-1.063459	-1.763694	0.774016
C	-1.287773	0.371577	0.683182
H	-0.798932	1.267789	0.304906
H	-1.376598	0.468784	1.771881
C	-2.692761	0.300767	0.123089
H	-3.188294	-0.687887	0.196937
O	2.651020	1.957956	-0.310212
O	-3.261965	1.237439	-0.356377
O	-0.257397	-1.071377	-0.992050
O	0.928201	-1.817983	-0.807082

TS(S7 → S13)

C	-2.815595	-0.675169	0.310873
H	-3.891932	-0.882525	0.439414
C	-2.481534	0.460670	-0.571429
H	-3.296563	0.888985	-1.142612
C	-1.262808	0.994505	-0.656460
H	-1.098149	1.845685	-1.311552
C	-0.038762	0.546898	0.077139
H	-0.251954	0.327323	1.125208
C	0.629306	-0.662558	-0.587309
H	0.635448	-0.539196	-1.673555
H	0.113869	-1.587765	-0.330528
C	2.083247	-0.774843	-0.159163
H	2.371708	0.313671	0.447126
O	-1.995140	-1.356277	0.878314
O	2.829742	-1.673073	-0.315684
O	0.874136	1.645373	0.008309
O	1.883069	1.421077	0.924636

TS(S7 → S14)

C	2.477701	-0.120965	0.391472
H	1.650109	-1.073739	0.130337
C	1.979019	1.074065	-0.339851
H	2.721906	1.771953	-0.708139
C	0.674840	1.220082	-0.547979
H	0.310003	2.068978	-1.116223
C	-0.355517	0.286112	0.049070
H	-0.092289	0.130170	1.105782
C	-1.767894	0.826428	-0.043196
H	-2.064395	0.981881	-1.081574
H	-1.811838	1.789774	0.476288
C	-2.769192	-0.091118	0.625032
H	-2.398905	-0.640708	1.512507
O	3.511535	-0.271145	0.941971
O	-3.901861	-0.209140	0.256797

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O -0.416663   -1.013205   -0.540186
O  0.838447   -1.531000   -0.799365
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TS(S15 → S18)

```
C -2.736491   -0.277231    0.472107
H -2.931660   -1.302974    0.832189
C -1.259660    0.126748    0.484242
H -1.051894    0.566792    1.467037
C -0.944123    1.081853   -0.634230
H -1.814393    1.382016   -1.206014
C  0.230500    1.589473   -0.979061
H  0.227266    2.268880   -1.825375
C  1.603515    1.430473   -0.383328
H  1.866165    2.356323    0.132831
H  2.313619    1.288309   -1.199762
C  1.830393    0.338685    0.628815
H  0.560124   -1.518538   -1.093863
O -3.607144    0.459891    0.119216
O  1.932113    0.471738    1.802923
O -0.481664   -1.074632    0.511061
O -0.511781   -1.684878   -0.703173
O  2.034647   -0.949895    0.123294
O  1.694575   -1.069825   -1.183110
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TS(S15 → S19)

```
C -2.564111    0.203412   -0.504294
H -2.807279    1.032266   -1.190577
C -1.111042    0.135390   -0.096189
H -0.602390   -0.634661   -0.942833
C -0.844644   -0.545514    1.195306
H -1.710098   -0.677082    1.833947
C  0.317092   -1.065546    1.575676
H  0.341933   -1.570405    2.535474
C  1.642658   -1.102764    0.858241
H  1.767472   -2.095887    0.417798
H  2.436227   -0.951760    1.589800
C  1.900802   -0.061786   -0.202417
H  0.868724    2.145717    0.629502
O -3.376792   -0.589640   -0.123794
O  2.537181    0.935461   -0.041840
O -0.459596    1.329929   -0.393544
O -0.086870    2.041982    0.781342
O  1.397995   -0.285177   -1.465698
O  0.445692   -1.260974   -1.485346
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TS(S15 → S20)

```
C -1.094108    1.503818    0.201759
H -0.108076    1.436517   -0.585227
C -1.748031    0.123418    0.381797
H -2.762124    0.260882    0.764892
C -0.889306   -0.616081    1.374170
H -1.278396   -0.625740    2.385259
C  0.288829   -1.182941    1.136665
H  0.799449   -1.644205    1.976053
C  1.038980   -1.253792   -0.170019
H  0.404999   -1.037134   -1.020905
H  1.484067   -2.242550   -0.272535
C  2.201148   -0.286841   -0.068796
H -2.993830   -1.719971   -1.463213
O -1.389312    2.491896    0.768500
O  3.242749   -0.518354    0.455460
O -1.776019   -0.419542   -0.919794
O -2.294643   -1.743178   -0.796118
O  2.006804    1.005584   -0.525372
O  0.919026    1.164434   -1.347397
```

TS(S15 → S21)

C	-3.099390	0.021882	-0.178636
H	-3.530409	0.950703	-0.588352
C	-1.673886	-0.270713	-0.647528
H	-1.768212	-0.862511	-1.569765
C	-0.897166	-1.037602	0.383023
H	-1.482304	-1.471522	1.185654
C	0.457857	-1.171018	0.394253
H	0.880033	-1.786551	1.181959
C	1.379332	-0.850538	-0.741922
H	0.901908	-0.217726	-1.490705
H	1.740235	-1.757408	-1.228589
C	2.618049	-0.125708	-0.242291
H	-0.221766	1.653990	0.455019
O	-3.703464	-0.712454	0.546202
O	3.684885	-0.089690	-0.753887
O	-1.056069	0.925397	-1.070240
O	-1.092415	1.816651	0.041988
O	2.422860	0.474390	0.984598
O	1.090670	0.597357	1.283012

TS(S16 → S37)

C	3.509968	0.445512	-0.152578
H	3.997630	1.435390	-0.142654
C	2.100235	0.414420	0.330177
H	1.699654	1.335002	0.738324
C	1.383121	-0.695688	0.209510
H	1.844780	-1.565327	-0.250798
C	-0.030662	-0.898867	0.660734
H	-0.060974	-1.688482	1.417464
C	-0.765662	0.337259	1.201068
H	-0.134433	0.866386	1.910872
H	-1.677663	0.024589	1.703089
C	-1.084640	1.277826	0.065546
H	-2.625523	-1.023543	-0.235277
O	4.103772	-0.526369	-0.537248
O	-0.482155	2.250140	-0.245330
O	-0.708328	-1.402640	-0.507934
O	-1.913866	-1.919746	-0.162715
O	-2.146200	0.902294	-0.765678
O	-3.067928	0.112972	-0.159563

TS(S16 → S38)

C	-3.694250	-0.703581	-0.198446
H	-4.197136	-1.662676	-0.410776
C	-2.211757	-0.720376	-0.282715
H	-1.741859	-1.659876	-0.549759
C	-1.515535	0.383842	-0.006445
H	-2.058638	1.277291	0.290844
C	-0.049423	0.491329	0.013868
H	0.295464	-0.084371	1.068435
C	0.776220	-0.323137	-0.968363
H	0.914513	0.211947	-1.906889
H	0.256292	-1.260267	-1.169134
C	2.154542	-0.675658	-0.448009
H	1.917387	2.685268	-0.204614
O	-4.335881	0.275994	0.078712
O	3.157739	-0.699144	-1.081861
O	0.276639	1.838229	0.076774
O	1.676803	1.912811	0.325192
O	2.220005	-0.951388	0.900436
O	0.986597	-1.154231	1.478568

TS(S16 → S40)

C	-3.392091	0.198826	0.176454
H	-4.252467	0.258931	0.863693

C	-2.081566	0.547319	0.748458
H	-2.039799	0.850384	1.789196
C	-0.942879	0.425456	-0.002215
H	-1.056460	0.283518	-1.073113
C	0.388570	0.962606	0.466608
H	0.244481	1.811693	1.140103
C	1.268334	-0.088010	1.162757
H	0.715183	-0.551258	1.977958
H	2.177615	0.372854	1.536994
C	1.662070	-1.097890	0.122413
H	2.878379	1.373495	-0.762808
O	-3.543804	-0.128137	-0.974992
O	2.754761	-1.309979	-0.296484
O	1.006313	1.412386	-0.733174
O	2.249521	2.007141	-0.384313
O	0.592028	-1.725894	-0.489349
O	-0.569014	-1.516698	0.188452

TS(S16 → S41)

C	3.005301	-0.334938	0.026658
H	3.769049	0.278607	0.531207
C	1.670105	-0.385166	0.705215
H	1.655294	-0.199099	1.773179
C	0.638663	-1.050341	0.090195
H	0.788052	-1.441453	-0.910907
C	-0.760724	-1.027088	0.614549
H	-0.906860	-1.725338	1.447672
C	-1.147686	0.393567	1.079796
H	-0.504783	0.704342	1.898480
H	-2.185756	0.399358	1.398730
C	-1.025822	1.305212	-0.113676
H	-3.160713	-0.525132	-0.651121
O	3.232187	-0.892979	-1.009829
O	-1.926609	1.598909	-0.837948
O	-1.539291	-1.434092	-0.501203
O	-2.913328	-1.329899	-0.166197
O	0.241675	1.704323	-0.473993
O	1.188703	1.491393	0.501213

TS(S17 → S40)

C	-2.886457	0.281320	0.493016
H	-2.292146	0.697633	1.326633
C	-2.171261	-0.044208	-0.739934
H	-2.764468	-0.486955	-1.530779
C	-0.812860	0.083171	-0.892467
H	-0.395339	-0.046355	-1.885216
C	0.080459	0.867146	0.046967
H	-0.454560	1.698914	0.509559
C	0.733423	0.007443	1.141019
H	-0.027705	-0.552938	1.681256
H	1.298116	0.634736	1.824586
C	1.707380	-0.909890	0.456346
H	2.757389	1.699259	-0.063778
O	-4.075086	0.109117	0.620363
O	2.891680	-0.908927	0.564624
O	1.074578	1.391227	-0.828176
O	1.937024	2.216632	-0.057228
O	1.138884	-1.728926	-0.502128
O	-0.220255	-1.748396	-0.408949

TS(S17 → S41)

C	-2.619256	-0.523432	-0.239799
H	-3.569030	0.030591	-0.319976
C	-1.775690	-0.158757	0.942202
H	-2.322249	0.207882	1.802934

C	-0.524004	-0.689921	1.154602
H	-0.086363	-0.632441	2.144697
C	0.424139	-1.078225	0.064056
H	0.153675	-2.027666	-0.407895
C	0.505429	0.012185	-1.027936
H	-0.439580	0.077853	-1.555441
H	1.296194	-0.247745	-1.725324
C	0.884567	1.306494	-0.365369
H	3.135146	-0.589338	-0.207289
O	-2.305298	-1.348154	-1.054106
O	1.991698	1.742400	-0.288638
O	1.661600	-1.196190	0.760686
O	2.697328	-1.455063	-0.171307
O	-0.106687	1.973268	0.328904
O	-1.381004	1.530089	0.062181

TS(S17 → S55)

C	3.298898	0.039877	0.321751
H	4.389902	0.198674	0.283263
C	2.560776	0.331832	-0.923709
H	3.115096	0.814360	-1.719520
C	1.281588	0.010985	-1.113391
H	0.805173	0.248296	-2.060184
C	0.388305	-0.663446	-0.116791
H	0.892715	-1.470130	0.413410
C	-0.205859	0.324402	0.910512
H	0.593848	0.924686	1.333976
H	-0.711541	-0.225014	1.699450
C	-1.149781	1.237011	0.172484
H	-2.256349	-1.291001	0.253704
O	2.777250	-0.351942	1.338837
O	-0.894596	2.297315	-0.292321
O	-0.670130	-1.220280	-0.922779
O	-1.469620	-2.012058	-0.167657
O	-2.419860	0.719787	-0.116676
O	-2.807097	-0.293303	0.696941

TS(S17 → S56)

C	-3.081326	-0.482606	-0.038824
H	-4.170377	-0.610726	0.090859
C	-2.658341	0.839995	-0.572502
H	-3.444726	1.453533	-0.998040
C	-1.399709	1.280246	-0.609376
H	-1.190223	2.221997	-1.107486
C	-0.231733	0.590587	-0.004780
H	-0.119907	-0.524324	-0.588599
C	1.135814	1.162807	-0.333132
H	1.409472	1.981273	0.332281
H	1.106357	1.526103	-1.362996
C	2.243644	0.132241	-0.255668
H	0.702870	-0.055116	2.714078
O	-2.325323	-1.384355	0.204563
O	3.338313	0.314669	0.170026
O	-0.479196	0.403514	1.343034
O	0.561263	-0.436887	1.837145
O	1.904428	-1.122735	-0.693941
O	0.707571	-1.165751	-1.385127

TS(S17 → S57)

C	-1.986520	-1.151138	-0.156985
H	-1.507857	-0.386253	-1.005918
C	-1.177538	-1.254219	1.079778
H	-1.725243	-1.584881	1.954859
C	0.125462	-0.993793	1.138511
H	0.638439	-1.110433	2.088860

C	1.007612	-0.552804	0.004005
H	0.652911	-0.932758	-0.951637
C	1.178674	0.978689	-0.061329
H	1.538223	1.245126	-1.055272
H	1.917549	1.273353	0.683017
C	-0.053780	1.786642	0.264240
H	3.907089	-0.701730	-0.442422
O	-3.044478	-1.646786	-0.344535
O	-0.154676	2.545241	1.174743
O	2.254851	-1.168084	0.293872
O	3.071559	-0.952484	-0.856858
O	-1.148952	1.659437	-0.565599
O	-0.976375	0.727341	-1.561724

TS(S24 → S28)

C	2.701353	-0.485104	-0.375902
H	2.986536	0.704367	-0.026197
C	1.178884	-0.517917	-0.706708
H	1.100444	-0.848120	-1.746351
C	0.583904	0.889680	-0.547761
C	-0.909426	0.951584	-0.286165
H	-1.218693	2.000367	-0.293238
C	-1.795536	0.114155	-1.188386
H	-1.336211	-0.832188	-1.476609
H	-2.165831	0.632151	-2.068909
C	-2.945822	-0.197442	-0.256131
H	0.150146	-0.819326	1.722192
O	3.450246	-1.382825	-0.459857
O	-4.036644	-0.593624	-0.489610
O	0.560994	-1.531567	0.038084
O	0.906963	-1.343474	1.404831
O	-2.562791	0.092715	1.030074
O	-1.177534	0.423942	1.023702
H	0.780305	1.448571	-1.469616
O	1.214787	1.579181	0.524110
O	2.496874	1.903709	0.119296

TS(S24 → S29)

C	-2.692000	-0.945321	0.766540
H	-3.733308	-1.012514	0.412250
C	-1.658824	-0.707444	-0.332215
H	-1.383851	-1.689795	-0.736970
C	-0.382164	-0.065195	0.181325
C	0.741574	-0.110181	-0.899598
H	0.306834	0.016812	-1.891019
C	1.854004	0.826174	-0.577777
H	1.315687	1.547549	0.462091
H	2.169381	1.610708	-1.254731
C	2.894302	-0.030683	0.041144
H	-2.322287	1.766734	-0.770543
O	-2.384022	-1.089260	1.912413
O	3.938564	0.245300	0.533476
O	-2.221042	-0.010159	-1.423477
O	-2.988346	1.073799	-0.904850
O	2.421280	-1.326532	0.052556
O	1.333930	-1.412404	-0.868724
H	-0.032144	-0.578224	1.081302
O	-0.637576	1.293916	0.470516
O	0.429503	1.792168	1.180729

TS(S24 → S30)

C	2.233695	-1.413953	-0.776103
H	1.677030	-1.938204	-1.577143
C	1.338168	-0.754242	0.272632
H	0.940956	-1.558824	0.903188

C	0.135351	-0.044177	-0.337360
C	-0.905939	0.327160	0.725754
H	-0.441130	0.835815	1.566743
C	-2.115788	1.033627	0.152226
H	-1.908651	1.661034	-0.711211
H	-2.642794	1.617450	0.906979
C	-2.976397	-0.143376	-0.252489
H	1.957646	1.772244	0.134089
O	3.423132	-1.410965	-0.731606
O	-3.916425	-0.202448	-0.970988
O	2.074729	0.067085	1.171700
O	2.758740	1.025895	0.473348
O	-2.460867	-1.281298	0.324690
O	-1.453203	-0.882068	1.258904
H	-0.326771	-0.713041	-1.069703
O	0.516948	1.101251	-1.111926
O	0.868092	2.119209	-0.271733

Unscaled Harmonic Vibrational Wavenumbers and Rotational constants (in cm^{-1}) at the M06-2X/TZVP Level of Theory

S5

Vibrational wavenumbers (cm^{-1}): 27, 61, 72, 87, 161, 167, 210, 266, 327, 357, 453, 510, 552, 597, 696, 737, 789, 897, 987, 1011, 1029, 1058, 1069, 1079, 1147, 1225, 1242, 1272, 1281, 1308, 1370, 1406, 1440, 1446, 1464, 1767, 1876, 1885, 2976, 3018, 3055, 3123, 3155, 3171, 3226

Rotational constants (cm^{-1}): A = 0.0807258, B = 0.0220296, C = 0.0198384

S6

Vibrational wavenumbers (cm^{-1}): 40, 56, 79, 88, 120, 150, 199, 207, 264, 320, 408, 522, 534, 646, 734, 760, 863, 890, 971, 1024, 1036, 1046, 1071, 1085, 1165, 1216, 1244, 1271, 1306, 1335, 1381, 1404, 1444, 1446, 1450, 1743, 1852, 1886, 2983, 3028, 3065, 3080, 3146, 3175, 3186

Rotational constants (cm^{-1}): A = 0.0913562, B = 0.0206593, C = 0.0182303

S7

Vibrational wavenumbers (cm^{-1}): 41, 71, 94, 122, 142, 192, 212, 247, 315, 398, 426, 454, 526, 654, 742, 772, 817, 921, 960, 1022, 1036, 1046, 1069, 1106, 1121, 1216, 1231, 1264, 1278, 1364, 1371, 1430, 1436, 1442, 1455, 1711, 1826, 1881, 2978, 3025, 3085, 3137, 3151, 3181, 3205

Rotational constants (cm^{-1}): A = 0.0605866, B = 0.0313870, C = 0.0226090

S15

Vibrational wavenumbers (cm^{-1}): 37, 58, 116, 138, 145, 168, 184, 213, 227, 287, 313, 396, 437, 462, 508, 562, 584, 614, 644, 707, 782, 837, 882, 951, 964, 1026, 1028, 1074, 1085, 1094, 1145, 1218, 1255, 1264, 1290, 1337, 1364, 1412, 1428, 1442, 1451, 1756, 1887, 1935, 3043, 3052, 3078, 3124, 3185, 3208, 3730

Rotational constants (cm^{-1}): A = 0.0671014, B = 0.0171125, C = 0.0159560

S16

Vibrational wavenumbers (cm^{-1}): 40, 50, 98, 126, 136, 148, 179, 206, 220, 252, 289, 395, 419, 464, 502, 525, 564, 593, 699, 744, 815, 864, 927, 958, 996, 1035, 1036, 1052, 1070, 1121, 1163, 1253, 1273, 1294, 1327, 1346, 1373, 1404, 1440, 1450, 1495, 1737, 1852, 1934, 3019, 3056, 3116, 3173, 3201, 3210, 3740

Rotational constants (cm^{-1}): A = 0.0380120, B = 0.0227381, C = 0.0159634

S17

Vibrational wavenumbers (cm^{-1}): 32, 62, 98, 115, 138, 144, 174, 222, 229, 261, 389, 404, 444, 483, 499, 524, 541, 593, 698, 759, 815, 850, 925, 952, 975, 1031, 1036, 1047, 1076, 1132, 1135, 1242, 1255, 1274, 1282, 1341, 1382, 1434, 1447, 1457, 1494, 1716, 1825, 1934, 3028, 3115, 3138, 3171, 3197, 3206, 3749

Rotational constants (cm^{-1}): A = 0.0399980, B = 0.0264343, C = 0.0192657

S24

Vibrational wavenumbers (cm^{-1}): 34, 58, 77, 122, 142, 159, 169, 199, 218, 234, 259, 319, 347, 389, 493, 499, 503, 534, 566, 640, 695, 735, 808, 856, 859, 910, 960, 966, 979, 1033, 1073, 1075, 1101, 1121, 1172, 1218, 1232, 1274, 1285, 1312, 1326, 1354, 1371, 1392, 1413, 1427, 1448, 1486, 1873, 1946, 3061, 3087, 3100, 3115, 3141, 3169, 3762

Rotational constants (cm^{-1}): A = 0.0397035, B = 0.0176312, C = 0.0165961

TS(S5 → S3+O_2)

Vibrational wavenumbers (cm^{-1}): i536, 58, 87, 97, 102, 137, 160, 181, 237, 311, 349, 407, 491, 516, 545, 637, 774, 826, 940, 995, 1006, 1018, 1048, 1072, 1149, 1174, 1236, 1266, 1306, 1317, 1430, 1437, 1465, 1484, 1486, 1640, 1824, 1862, 2985, 3012, 3079, 3143, 3168, 3189, 3191

Rotational constants (cm^{-1}): A = 0.0628285, B = 0.0302009, C = 0.0276618

TS(S5 → S8)

Vibrational wavenumbers (cm^{-1}): i1606, 45, 97, 144, 189, 223, 262, 281, 353, 380, 444, 492, 586, 599, 617, 746, 780, 813, 880, 959, 990, 1027, 1032, 1060, 1073, 1088, 1170, 1211, 1268, 1278, 1292, 1353, 1413, 1428, 1472, 1578, 1757, 1881, 1960, 3042, 3060, 3086, 3150, 3178, 3204

Rotational constants (cm^{-1}): A = 0.0852570, B = 0.0281078, C = 0.0246147

TS(S5 → S9)

Vibrational wavenumbers (cm^{-1}): i662, 48, 68, 90, 114, 196, 209, 257, 337, 408, 470, 516, 567, 614, 736, 769, 821, 865, 922, 936, 1018, 1031, 1055, 1067, 1079, 1120, 1217, 1248, 1254, 1305, 1326, 1393, 1407, 1420, 1453, 1512, 1868, 1881, 3031, 3050, 3072, 3074, 3135, 3162, 3210

Rotational constants (cm^{-1}): A = 0.1454993, B = 0.0216697, C = 0.0204251

TS(S5 → S10)

Vibrational wavenumbers (cm^{-1}): i727, 29, 65, 84, 114, 127, 182, 216, 272, 342, 407, 509, 573, 633, 675, 774, 788, 859, 924, 988, 1023, 1036, 1057, 1083, 1102, 1131, 1213, 1244, 1280, 1289, 1330, 1407, 1425, 1440, 1442, 1551, 1879, 1883, 2970, 3012, 3033, 3082, 3100, 3200, 3216

Rotational constants (cm^{-1}): A = 0.1004311, B = 0.0207677, C = 0.0195585

TS(S6 → S3+O_2)

Vibrational wavenumbers (cm^{-1}): i513, 46, 52, 76, 85, 133, 146, 224, 239, 253, 310, 315, 457, 512, 591, 766, 789, 813, 882, 958, 1007, 1021, 1038, 1063, 1090, 1188, 1221, 1272, 1313, 1335, 1433, 1442, 1447, 1461, 1498, 1610, 1813, 1881, 2986, 3010, 3021, 3094, 3178, 3200, 3215

Rotational constants (cm^{-1}): A = 0.0805837, B = 0.0208788, C = 0.0182990

TS(S6 → S9)

Vibrational wavenumbers (cm^{-1}): i736, 50, 62, 86, 130, 165, 228, 245, 318, 392, 413, 484, 577, 670, 720, 755, 821, 897, 928, 971, 1001, 1026, 1045, 1071, 1115, 1149, 1222, 1237, 1276, 1281, 1352, 1386, 1434, 1440, 1445, 1535, 1842, 1884, 2980, 3041, 3048, 3062, 3139, 3178, 3219

Rotational constants (cm^{-1}): A = 0.1360918, B = 0.0200692, C = 0.0185945

TS(S6 → S11)

Vibrational wavenumbers (cm^{-1}): i1904, 47, 90, 105, 123, 199, 217, 259, 326, 384, 422, 453, 480, 590, 608, 766, 802, 856, 943, 974, 987, 1022, 1052, 1056, 1093, 1127, 1160, 1238, 1273, 1299, 1327, 1363, 1392, 1445, 1450, 1659, 1731, 1852, 1969, 3013, 3071, 3083, 3150, 3170, 3176

Rotational constants (cm^{-1}): A = 0.0999171, B = 0.0198204, C = 0.0168607

TS(S6 → S12)

Vibrational wavenumbers (cm^{-1}): i1031, 53, 74, 85, 112, 162, 190, 211, 264, 329, 418, 447, 589, 672, 733, 782, 814, 871, 940, 970, 1022, 1035, 1040, 1071, 1132, 1166, 1242, 1269, 1294, 1317, 1360, 1421, 1440, 1441, 1449, 1534, 1783, 1881, 2983, 3035, 3069, 3075, 3144, 3212, 3225

Rotational constants (cm^{-1}): A = 0.1024892, B = 0.0210346, C = 0.0189124

TS(S7 → S4 + O_2)

Vibrational wavenumbers (cm^{-1}): i506, 34, 59, 77, 81, 143, 179, 184, 235, 261, 328, 384, 480, 521, 539, 719, 748, 804, 900, 973, 1016, 1027, 1040, 1065, 1090, 1194, 1223, 1272, 1280, 1404, 1435, 1439, 1465, 1469, 1508, 1605, 1793, 1887, 2975, 3039, 3078, 3106, 3161, 3182, 3200

Rotational constants (cm^{-1}): A = 0.0594515, B = 0.0253769, C = 0.0220920

TS(S7 → S9)

Vibrational wavenumbers (cm^{-1}): i690, 48, 63, 131, 147, 188, 250, 284, 325, 374, 427, 506, 555, 646, 730, 839, 851, 874, 904, 964, 981, 1015, 1021, 1052, 1104, 1138, 1177, 1259, 1286, 1346, 1371, 1390, 1426, 1434, 1465, 1494, 1837, 1868, 3026, 3048, 3053, 3086, 3153, 3171, 3228

Rotational constants (cm^{-1}): A = 0.0892924, B = 0.0277846, C = 0.0261374

TS(S7 → S12)

Vibrational wavenumbers (cm^{-1}): i951, 51, 70, 88, 129, 169, 221, 237, 288, 335, 410, 464, 533, 627, 726, 766, 796, 887, 923, 964, 1017, 1035, 1069, 1079, 1142, 1166, 1225, 1262, 1280, 1361, 1390, 1428, 1438, 1444, 1458, 1520, 1783, 1884, 2977, 3052, 3062, 3070, 3148, 3202, 3217

Rotational constants (cm^{-1}): A = 0.0631717, B = 0.0287115, C = 0.0230730

TS(S7 → S13)

Vibrational wavenumbers (cm^{-1}): i1841, 63, 93, 120, 159, 204, 236, 314, 370, 402, 424, 446, 498, 533, 618, 742, 811, 836, 948, 966, 970, 1034, 1048, 1065, 1114, 1121, 1124, 1220, 1256, 1265, 1344, 1360, 1429, 1433, 1457, 1673, 1717, 1827, 1966, 3025, 3073, 3121, 3149, 3167, 3193

Rotational constants (cm^{-1}): A = 0.0691568, B = 0.0286181, C = 0.0230002

TS(S7 → S14)

Vibrational wavenumbers (cm^{-1}): i2082, 51, 71, 113, 138, 170, 262, 278, 308, 370, 420, 446, 522, 563, 623, 690, 743, 799, 905, 979, 1023, 1033, 1051, 1108, 1124, 1150, 1208, 1240, 1297, 1311, 1363, 1382, 1417, 1438, 1448, 1493, 1708, 1884, 1945, 2995, 3016, 3056, 3128, 3179, 3214

Rotational constants (cm^{-1}): A = 0.1063956, B = 0.0215099, C = 0.0199248

TS(S15 → S18)

Vibrational wavenumbers (cm^{-1}): i2218, 46, 80, 103, 121, 144, 191, 249, 267, 329, 363, 409, 450, 503, 561, 577, 605, 654, 686, 716, 792, 819, 871, 898, 946, 986, 998, 1037, 1072, 1104, 1140, 1164, 1183, 1272, 1283, 1302, 1347, 1388, 1417, 1441, 1461, 1671, 1765, 1890, 1924, 3036, 3075, 3082, 3124, 3170, 3216

Rotational constants (cm^{-1}): A = 0.0528539, B = 0.0231950, C = 0.0211877

TS(S15 → S19)

Vibrational wavenumbers (cm^{-1}): i1776, 71, 90, 131, 144, 176, 201, 236, 256, 297, 349, 380, 407, 424, 476, 516, 572, 587, 632, 693, 731, 786, 851, 900, 963, 986, 1003, 1024, 1052, 1126, 1152, 1160, 1177, 1260, 1289, 1313, 1381, 1407, 1433, 1462, 1473, 1541, 1736, 1854, 1888, 3040, 3091, 3146, 3167, 3186, 3722

Rotational constants (cm^{-1}): A = 0.0488988, B = 0.0248215, C = 0.0236243

TS(S15 → S20)

Vibrational wavenumbers (cm^{-1}): i1790, 54, 72, 98, 121, 173, 187, 196, 213, 248, 342, 378, 417, 430, 492, 500, 513, 604, 609, 719, 748, 771, 865, 902, 987, 1000, 1023, 1042, 1056, 1126, 1132, 1162, 1239, 1269, 1284, 1293, 1306, 1324, 1385, 1414, 1426, 1500, 1745, 1908, 1964, 3098, 3127, 3180, 3198, 3220, 3824

Rotational constants (cm^{-1}): A = 0.0421221, B = 0.0244266, C = 0.0200392

TS(S15 → S21)

Vibrational wavenumbers (cm^{-1}): i565, 45, 60, 107, 137, 168, 202, 226, 249, 265, 331, 377, 440, 500, 561, 598, 615, 646, 670, 709, 794, 829, 844, 940, 966, 978, 1020, 1040, 1074, 1089, 1144, 1152, 1224, 1265, 1271, 1307, 1331, 1416, 1441, 1458, 1478, 1581, 1884, 1936, 3039, 3043, 3094, 3147, 3176, 3205, 3629

Rotational constants (cm^{-1}): A = 0.0714161, B = 0.0172870, C = 0.0166709

TS(S16 → S37)

Vibrational wavenumbers (cm^{-1}): i2167, 55, 77, 105, 121, 176, 210, 215, 250, 310, 355, 402, 432, 505, 527, 570, 592, 607, 740, 761, 839, 850, 859, 903, 974, 999, 1039, 1043, 1053, 1132, 1160, 1170, 1198, 1238, 1292, 1339, 1358, 1361, 1396, 1446, 1499, 1636, 1743, 1851, 1929, 3038, 3095, 3123, 3175, 3178, 3225

Rotational constants (cm^{-1}): A = 0.0572059, B = 0.0188374, C = 0.0155798

TS(S16 → S38)

Vibrational wavenumbers (cm^{-1}): i1840, 52, 61, 88, 116, 140, 182, 206, 222, 225, 261, 287, 376, 409, 424, 533, 547, 572, 589, 665, 788, 814, 859, 917, 969, 994, 1029, 1045, 1050, 1093, 1144, 1209, 1241, 1256, 1298, 1322, 1330, 1371, 1435, 1439, 1450, 1565, 1699, 1843, 1920, 3024, 3098, 3157, 3184, 3189, 3856

Rotational constants (cm^{-1}): A = 0.0586816, B = 0.0163036, C = 0.0147799

TS(S16 → S40)

Vibrational wavenumbers (cm^{-1}): i746, 48, 70, 78, 123, 148, 185, 244, 289, 295, 329, 351, 423, 436, 502, 531, 547, 605, 741, 764, 789, 844, 925, 947, 963, 1005, 1030, 1036, 1068, 1103, 1154, 1162, 1256, 1272, 1280, 1291, 1377, 1385, 1424, 1437, 1475, 1555, 1791, 1918, 3028, 3088, 3123, 3189, 3195, 3202, 3799

Rotational constants (cm^{-1}): A = 0.0529970, B = 0.0212400, C = 0.0173917

TS(S16 → S41)

Vibrational wavenumbers (cm^{-1}): i605, 54, 80, 107, 124, 188, 213, 229, 279, 299, 363, 411, 452, 480, 519, 525, 552, 602, 736, 756, 803, 862, 908, 933, 954, 989, 1026, 1037, 1086, 1099, 1131, 1161, 1260, 1265, 1272, 1278, 1365, 1380, 1433, 1443, 1501, 1577, 1862, 1900, 3046, 3047, 3141, 3180, 3204, 3212, 3755

Rotational constants (cm^{-1}): A = 0.0509399, B = 0.0235413, C = 0.0188614

TS(S17 → S40)

Vibrational wavenumbers (cm^{-1}): i737, 51, 82, 87, 131, 173, 209, 246, 276, 290, 328, 375, 411, 425, 498, 542, 557, 603, 686, 770, 801, 837, 904, 932, 970, 1017, 1031, 1048, 1079, 1098, 1156, 1169, 1229, 1261, 1292, 1346, 1388, 1397, 1430, 1458, 1477, 1546, 1776, 1919, 3012, 3111, 3123, 3191, 3205, 3217, 3787

Rotational constants (cm^{-1}): A = 0.0515290, B = 0.0208528, C = 0.0172900

TS(S17 → S41)

Vibrational wavenumbers (cm^{-1}): i603, 66, 87, 131, 150, 192, 197, 260, 266, 312, 356, 415, 454, 463, 503, 521, 537, 600, 713, 786, 800, 861, 899, 922, 948, 978, 1005, 1034, 1059, 1088, 1106, 1148, 1231, 1262, 1267, 1318, 1378, 1423, 1434, 1441, 1493, 1542, 1848, 1900, 3043, 3091, 3143, 3193, 3206, 3210, 3749

Rotational constants (cm^{-1}): A = 0.0457283, B = 0.0283883, C = 0.0213201

TS(S17 → S55)

Vibrational wavenumbers (cm^{-1}): i2222, 57, 77, 101, 136, 163, 226, 241, 269, 338, 376, 435, 453, 501, 504, 552, 591, 618, 725, 785, 818, 853, 854, 915, 961, 973, 1025, 1040, 1052, 1111, 1157, 1174, 1194, 1235, 1258, 1278, 1348, 1378, 1434, 1457, 1494, 1638, 1718, 1825, 1931, 3026, 3141, 3162, 3176, 3204, 3216

Rotational constants (cm^{-1}): A = 0.0530991, B = 0.0215459, C = 0.0187790

TS(S17 → S56)

Vibrational wavenumbers (cm^{-1}): i1877, 51, 82, 97, 109, 125, 176, 199, 221, 231, 275, 339, 386, 412, 426, 532, 543, 578, 604, 679, 742, 834, 856, 919, 934, 993, 1029, 1038, 1055, 1083, 1152, 1175, 1219, 1241, 1279, 1306, 1367, 1416, 1437, 1443, 1457, 1558, 1708, 1849, 1912, 3027, 3081, 3144, 3164, 3187, 3853

Rotational constants (cm^{-1}): A = 0.0581229, B = 0.0207457, C = 0.0204825

TS(S17 → S57)

Vibrational wavenumbers (cm^{-1}): i1525, 51, 90, 95, 138, 165, 180, 190, 221, 257, 322, 372, 394, 421, 493, 528, 543, 589, 598, 668, 712, 793, 861, 886, 999, 1018, 1034, 1061, 1118, 1122, 1140, 1166, 1226, 1262, 1277, 1317, 1354, 1389, 1408, 1444, 1466, 1474, 1728, 1910, 1928, 3093, 3154, 3169, 3179, 3204, 3837

Rotational constants (cm^{-1}): A = 0.0360032, B = 0.0254790, C = 0.0191076

TS(S24 → S28)

Vibrational wavenumbers (cm^{-1}): i1852, 58, 63, 93, 146, 169, 185, 220, 228, 276, 316, 321, 369, 414, 441, 470, 520, 532, 568, 594, 686, 692, 714, 831, 858, 867, 890, 921, 979, 1032, 1046, 1062, 1078, 1100, 1129, 1139, 1190, 1218, 1232, 1247, 1284, 1354, 1368, 1384, 1404, 1428, 1453, 1476, 1664, 1956, 1992, 3072, 3100, 3104, 3114, 3173, 3741

Rotational constants (cm^{-1}): A = 0.0466339, B = 0.0150307, C = 0.0136007

TS(S24 → S29)

Vibrational wavenumbers (cm^{-1}): i1762, 47, 62, 93, 104, 138, 155, 187, 222, 241, 307, 326, 385, 393, 439, 504, 513, 546, 598, 636, 645, 699, 723, 788, 839, 894, 922, 950, 962, 996, 1001, 1047, 1078, 1098, 1101, 1128, 1152, 1173, 1194, 1251, 1301, 1322, 1335, 1352, 1372, 1391, 1422, 1436, 1587, 1887, 1920, 3052, 3075, 3121, 3155, 3200, 3788

Rotational constants (cm^{-1}): A = 0.0431208, B = 0.0144417, C = 0.0139923

TS(S24 → S30)

Vibrational wavenumbers (cm^{-1}): i2850, 48, 67, 82, 112, 150, 181, 193, 219, 298, 321, 327, 357, 394, 465, 511, 545, 582, 688, 691, 728, 749, 796, 856, 874, 906, 943, 974, 999, 1021, 1044, 1057, 1066, 1084, 1130, 1142, 1165, 1188, 1224, 1272, 1311, 1324, 1342, 1371, 1391, 1416, 1433, 1468, 1479, 1906, 1951, 2971, 3078, 3107, 3110, 3175, 3179

Rotational constants (cm^{-1}): A = 0.0464668, B = 0.0144994, C = 0.0131588