Theoretical analysis of QOOH combustion reaction pathways

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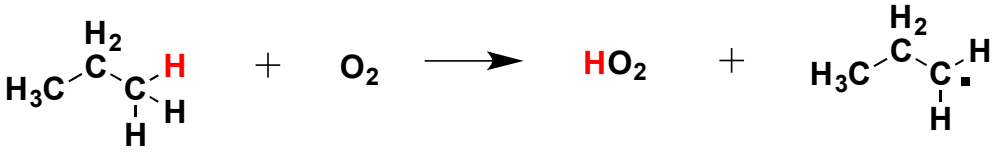
Abstract

QOOH radicals are key intermediates in the chain of reactions leading to the autoignition of hydrocarbons and oxygenated organic compounds. They are thought to undergo two main reactions: OH elimination to form a cyclic ether and HO_2 elimination to form an alkene. However, theoretical analysis of various substituted hydroperoxyalkyl radicals has found two new pathways: OH transfer and internal H abstraction assisted OH elimination. To determine the importance of these new pathways, their barrier heights for several substituted alkanes were calculated using various quantum chemical theories and compared to those of the well-known pathways. Several cases revealed possible competition with the well-known pathways. Rate coefficients were calculated for propyl systems but further studies will need to complete rate coefficients and branching fractions for all systems analyzed to understand these new reactions' role in autoignition.

Introduction

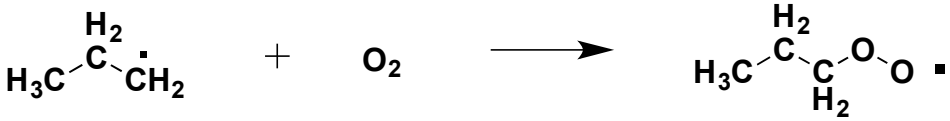
The need to increase engine efficiencies and lower unwanted emissions has resulted in recent attention on low-temperature hydrocarbon oxidation.[1-7] Engines employing low-temperature hydrocarbon oxidation (500-1900 K) utilize lower fuel concentrations compared to gasoline and diesel engines, effectively reducing soot formation, while the lower temperatures eliminate nitrogen oxides that are produced above 2000 K in gasoline and diesel engines.[8] Rather than spark ignition, these low-temperature hydrocarbon oxidation engines rely on autoignition prompted by compression.

Autoignition chemistry is driven by chemical chain propagation. The initial reaction proceeds via formation of an alkyl radical (R) from an alkane fuel molecule (RH) and oxygen



RH R·

From here, R reacts with oxygen to form an alkylperoxy radical (ROO)



R· ROO·

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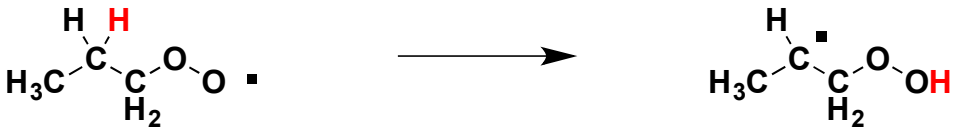
While ROO can undergo direct elimination to form an alkene + HO_2, it can also isomerize to form QOOH, a hydroperoxy alkyl radical



ROO ▪ ▪ QOOH

QOOH is a very important species because it is very unstable, and therefore very reactive. For this reason, QOOH formation leads to chain propagation and chain branching, which are ultimately responsible for autoignition. However, these steps comprise less than half of what is accepted as the autoignition pathway (Figure 1). From here, these reactions get very complicated.

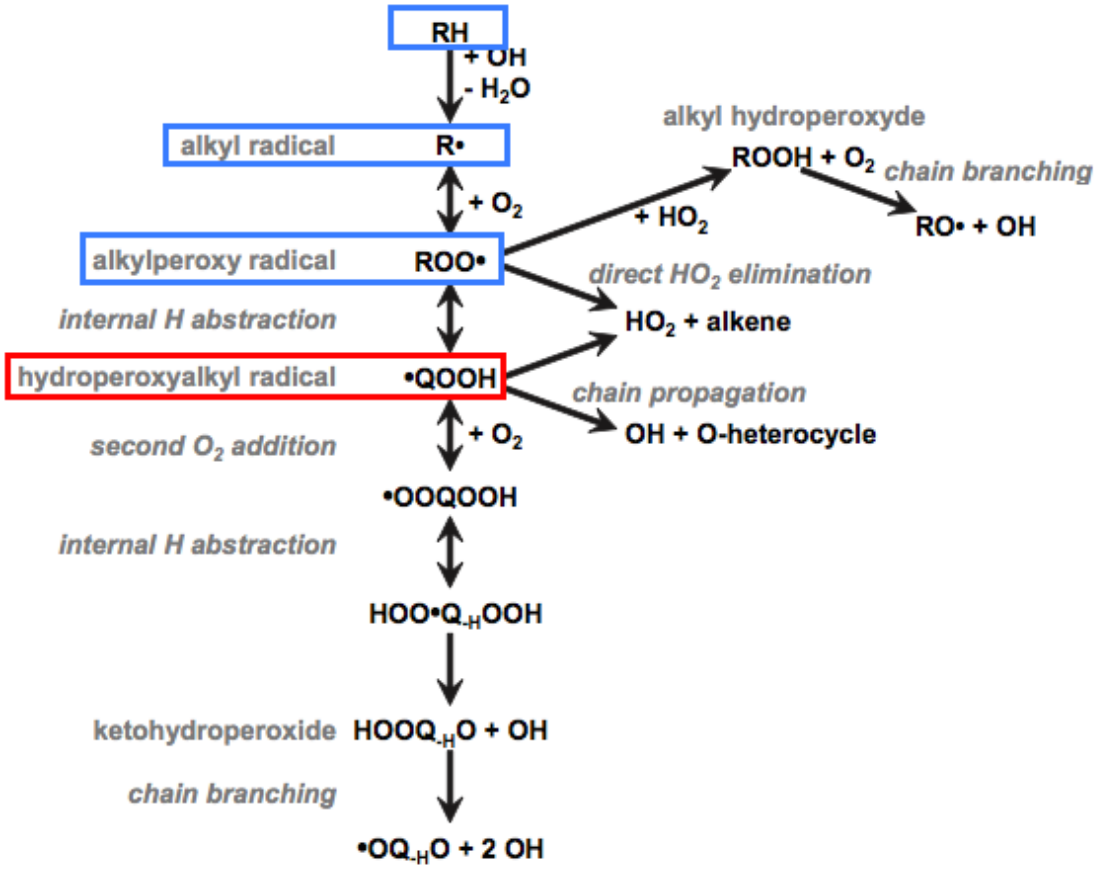


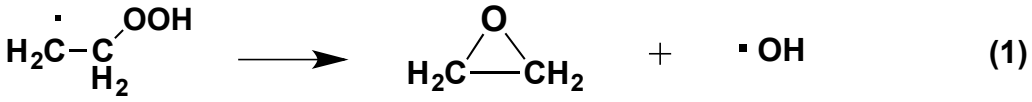
Figure 1. Schematic mechanism for low-temperature hydrocarbon oxidation and autoignition chemistry. Figure adopted from Zádor, Taatjes, and Fernandes 2011.[7]

In order to optimize new fuel or engine models, these reactions must be fully explored. These elementary reactions, however, are very hard to observe experimentally due to fast propagation—making it easy to miss important pathways or short-lived

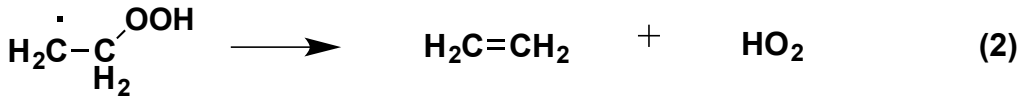
intermediates. In this sense, theoretical computations can help characterize these complicated pathways.

KinBot is a software that can predict gas-phase combustion reactions—allowing the modeling of several reaction pathways in much less time and with fewer holes that may be found experimentally or using less efficient computational methods.

As an overview, QOOH radicals are generally thought to undergo OH elimination to form a cyclic ether (1) or HO_2 elimination to form an alkene (2).

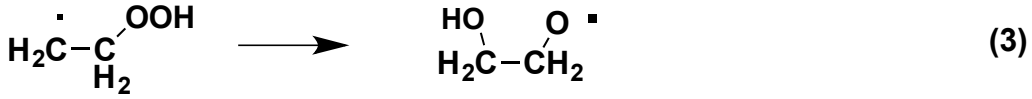


(1)

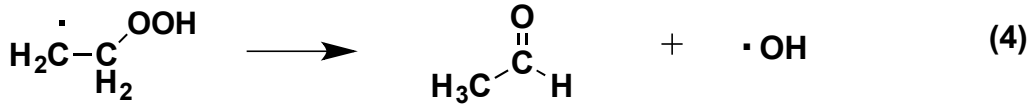


(2)

However, KinBot found two new reactions that have not yet been observed or investigated computationally—OH transfer (3) and internal H abstraction assisted OH elimination (4).



(3)



(4)

While DeSain et al.[2], Miller et al.[6], and Goldsmith et al.[3] report direct aldehyde + OH formation from RO_2, no studies have observed these products originating from QOOH as a reactant. Both the OH and H transfer found have the potential to contribute to autoignition. To understand whether these findings are specific to just certain QOOH radicals and how the energy of these new pathways compares to the already known ones, the barrier heights for several substituted alkanes were calculated using various quantum chemical theories.

Though barrier heights can suggest a lot about a given reaction, kinetics are required to understand the entire scope of a reaction. Both OH and H transfer reaction pathways introduced generate chain-propagating products that may speed up the autoignition process. To optimize fuel and engine models, the rate of these reactions must be known. As propane has received considerable attention as a possible prototype for low-temperature hydrocarbon oxidation,[1] rate coefficients were calculated for propyl systems undergoing OH and H transfer to better contribute to the prototype already in place.

Methods

To determine the barrier height for various substituted alkanes (Figure 2), saddle points were located using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), and CBS-CB3 quantum chemical theories using the Gaussian 09 program package. The saddle points were proven to connect the proposed reactants and products by following the pathways along the intrinsic reaction coordinates (IRC). Besides the above methods, highly accurate energies were calculated at the UCCSD(T)-F12/cc-pV*n*Z//M06-2X/6-311++G(d,p) level of theory for each species, where n = T or Q.

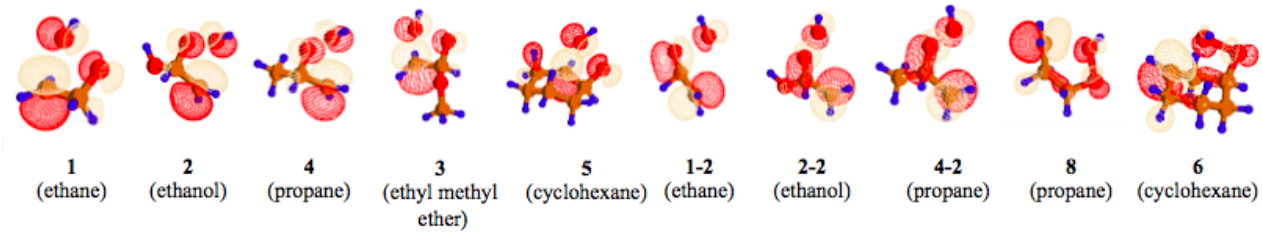


Figure 2. Geometries and highest occupied molecular orbitals (HOMOs) of tested transition states for various QOOH species. Species denoted with '-2' undergo H-transfer (reaction 4), the others OH-transfer (reaction 3).

Species 4, 4-2, and 8 were investigated further, in addition to species 9 (CH_3CHCH_2OOH undergoing OH transfer) and 9-22 (CH_3CHCH_2OOH undergoing H transfer) to develop a greater understanding of the OH and H transfer reaction pathways for propyl systems. Lowest energy conformers for 4reactant/4-2reactant, 4-2product and 8reactant were adapted from Goldsmith et al.[3] (QOOH-3, acetone + OH, and QOOH-1, respectively) and studied using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), CBS-CB3, and UCCSD(T)-F12/cc-pVQZ//M06-2X/6-311++G(d,p) levels of theory. The lowest energy conformer for 9reactant and 9-22reactant was found to be the 9-22reactant conformer generated in this work, as it was lower in energy than its respective QOOH-2 conformer from Goldsmith et al.[3] The energy difference at the M06-2X level of theory was 0.486 kcal/mol. For transition states and remaining products not discussed in Goldsmith et al.[3], 3^n possible conformers were generated for each species, where n is the number of dihedral angles, and optimized using M06-2X/6-311++G(d,p) level of theory. Lowest energy conformers were selected and reoptimized using the above methods. The potential energy surfaces for propyl systems undergoing OH and H transfer were similarly compared to those undergoing the well-known cyclic ether and alkene formation pathways.

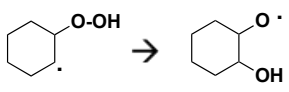
Hindered rotor energy scans were calculated for each propyl product using KinBot/Gaussian, whereas the rotors for propyl transition states were generated manually and run in Gaussian. These rotor energies, along with geometries and frequencies optimized at the M06-2X/6-311++G(d,p) level of theory for each transition state were incorporated into the propane master-equation provided by Michael P. Burke (Columbia University) to calculate temperature and pressure dependent rate coefficients. The master equation is equivalent to the one published by Burke et al.[3] 2015. The master equation was run using the PAPER code of Argonne National Laboratory.

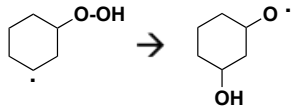
Results and Discussion

Energies for new OH and H transfer reaction pathways were calculated for ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems using B3LYP/6-311++G(d,p), M06-2X/6-

311++G(d,p), CBS-CB3, and UCCSD(T)-F12/cc-pV*n*Z//M06-2X/6-311++G(d,p) levels of theory (*n* = D, T or Q). Energies for transition states and products are listed in Table 1 and 2, respectively.

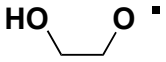
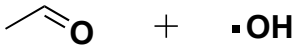
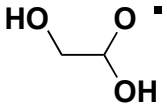
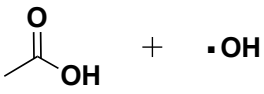
Table 1. Transition state energies for ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems.

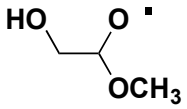
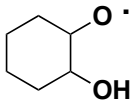
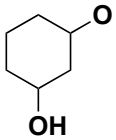
		Relative energy[a]				
Species	Reaction	B3LYP[b]	M06-2X[b]	CBS-QB3	UCCSD(T)-F12	T1 Diagnostic
TS1	$CH_2CH_2OOH \rightarrow CH_2(OH)CH_2O$	24.6	37.8	30.7	30.1[c]	0.068
TS1-2	$CH_2CH_2OOH \rightarrow CH_3CHO + OH$	21.3	32.6	30.7	28.8[d]	0.071
TS2	$CH_2CH(OOH)OH \rightarrow CH_2(OH)CH(O)OH$	23.8	36.7	25.2	28.4[e]	0.068
TS2-2	$CH_2CH(OOH)OH \rightarrow CH_3COOH + OH$	17.9	30.0		26.0[d]	0.066
TS3	$CH_2CH(OOH)OCH_3 \rightarrow CH_2(OH)CH(O)OCH_3$	27.0	39.8	26.2	31.0[e]	0.055
TS5		20.1	31.6	21.2	20.4[d]	0.088

TS6		21.8	28.3	21.8	20.3[d]	0.067

[a]All energies are relative to respective reactant in kcal/mol.
[b]Present work employing 6-311++G(d,p) basis set.
[c]Present work employing cc-pVQZ//M06-2X/6-311++G(d,p) basis set and geometry.
[d]Present work employing cc-pVDZ//M06-2X/6-311++G(d,p) basis set and geometry.
[e]Present work employing cc-pVTZ//M06-2X/6-311++G(d,p) basis set and geometry.

Table 2. Product energies for ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems.

		Relative Energy[a]	
Species	Structure	B3LYP[b]	M06-2X[b]
1product		-51.0	-52.1
1-2product		-50.8[c]	-49.4
2product		-54.2	-54.3
2-2product		-70.1[c]	-67.7

3product		-57.0	-56.0
5product		-49.7	-51.3
6product		-49.4	-57.6

[a]All energies are relative to respective reactant in kcal/mol.
[b]Present work employing 6-311++G(d,p) basis set.
[c]Products not calculated separately.

Overall, the transition state barrier for H transfer reaction pathways were lower in energy than those undergoing OH transfer for the above systems, while the latter reaction pathways were more exothermic. The new reaction pathways for ethyl and cyclohexyl systems were compared to the more common reaction pathways (Figure 3 and 4).

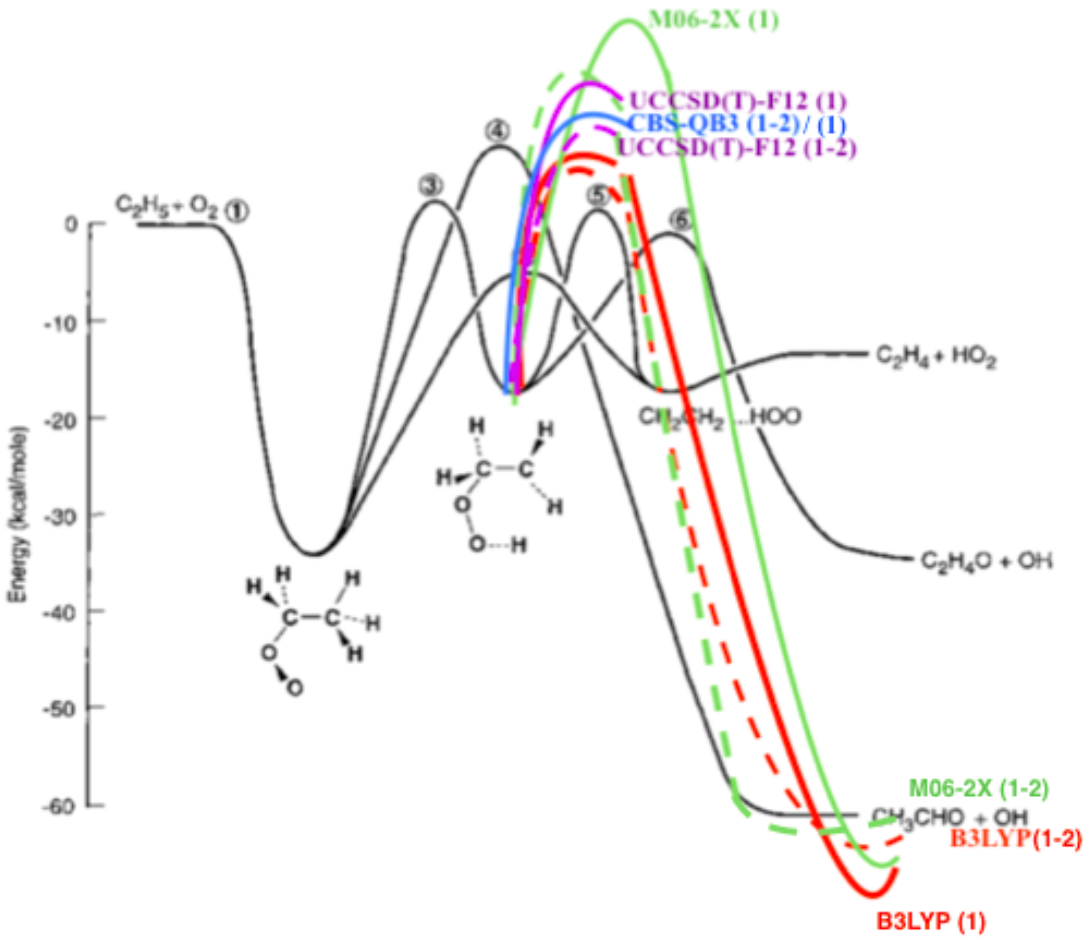


Figure 3. Schematic potential energy surfaces comparing calculated energy barriers of new OH transfer (1) and H transfer (1-2) pathways and those of common HO_2 and OH elimination pathways from CH_2CH_2OOH (1 and 1-2) using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), and UCCSD(T)-F12 levels of theory (barriers for 1 and 1-2 were calculated at cc-pVQZand cc-pVDZ basis sets, respectively). The drawn barrier heights are given relative to the ethyl + O_2 entrance channel: $TS1_{B3LYP}$= 7.6, $TS1_{M06\text{-}2x}$=20.8, $TS1_{CBS\text{-}QB3}$=13.7 $TS1_{UCCSD}$=13.0; $TS1\text{-}2_{B3LYP}$= 4.3, $TS1\text{-}2_{M06\text{-}2x}$=15.6, $TS1\text{-}2_{CBS\text{-}QB3}$=13.7, and $TS1\text{-}2_{UCCSD}$=11.8. $1product_{B3LYP}$= -68.0, $1product_{M06\text{-}2x}$= -69.1; $1\text{-}2product_{B3LYP}$= -67.8, $1\text{-}2product_{M06\text{-}2x}$= -66.4. Base figure adapted from Miller, Klippenstein, and Robertson 2000.[6]

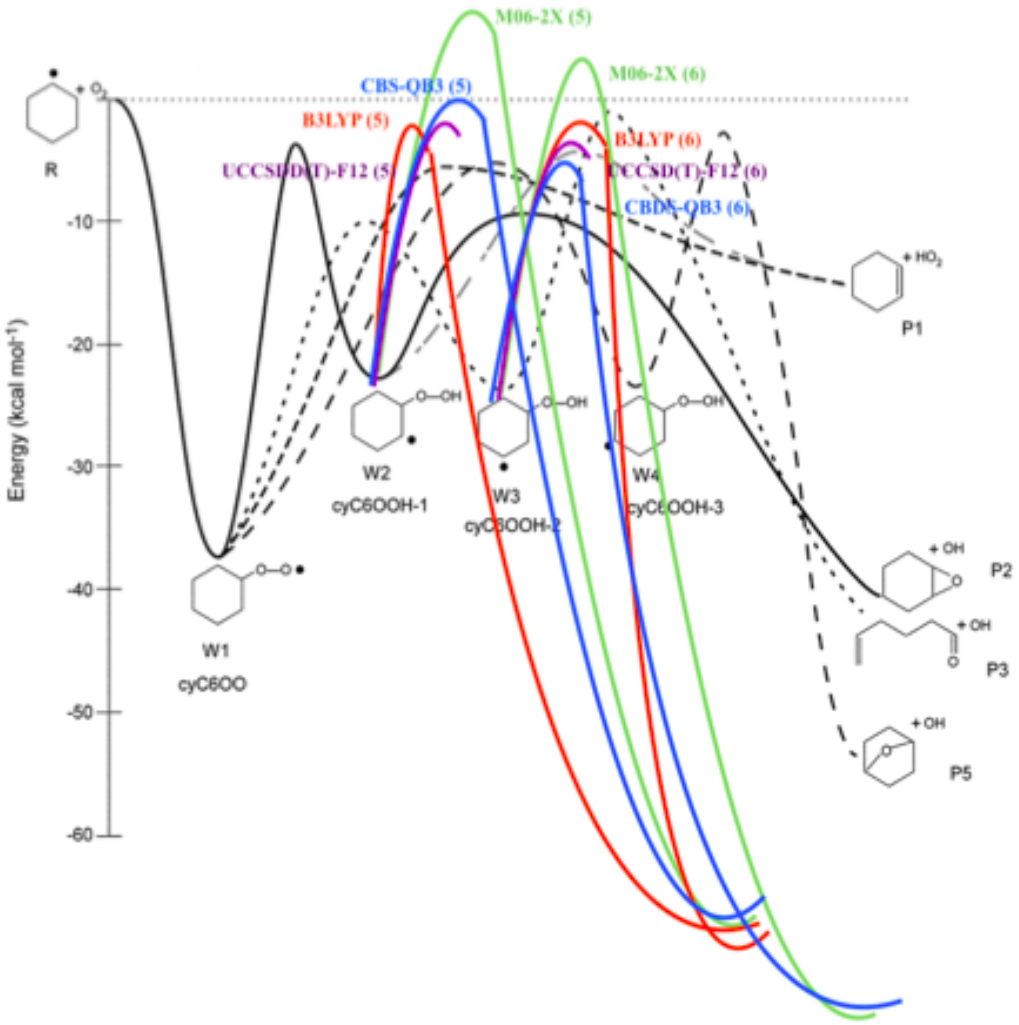


Figure 4. Schematic potential energy surfaces comparing calculated energy barriers of new OH transfer pathway and those of common HO_2 and OH elimination pathways from cyC_6OOH-1 (5) and cyC_6OOH-2 (6) using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), CBS-CB3, and UCCSD(T)-F12/cc-pVDZ//M06-2X/6-31++G(d,p) levels of theory. Drawn barriers represent E + ZPE values in kcal/mol. The barrier heights relative to the cyclohexyl + O_2 entrance channel: $Ts5_{B3LYP}$= -1.9, $Ts5_{M06\text{-}2x}$=9.6, $Ts5_{CBS\text{-}QB3}$= -0.8, $Ts5_{UCCSD}$= -1.6; $Ts6_{B3LYP}$= -1.4, $Ts6_{M06\text{-}2x}$=5.1, $Ts6_{CBS\text{-}QB3}$= -1.4, and $Ts6_{UCCSD}$= -2.9. $5product_{B3LYP}$= -71.7, $5product_{M06\text{-}2x}$= -73.3; $6product_{B3LYP}$= -72.6, $6product_{M06\text{-}2x}$= -80.8. Base figure adapted from Knepp et al.[5]

While the OH transfer and H transfer reaction pathways were much higher in energy compared to the well-known reaction pathways for the ethyl system (1 and 1-2) and TS5, there is a good comparison between those of TS6 and the well-known pathways. However, both OH transfers for TS5 and TS6 are extremely exothermic, suggesting the likelihood of chain propagation. The product of TS6 is likely to dissociate into P3 on the cyclohexyl PES (Figure 4), while we have not investigated the likely dissociation pathways for the product of TS5.

As a general observation, the OH transfer is competitive in γ-QOOH radicals likely because the OH transfer involves a 5-member ring TS, which has significantly less ring strain than the related 4-membered-ring cyclic ether formation pathway in this case.

All of the energies at the saddle points exhibit unusually large T1 diagnostic values (meaning high multi-reference character), which means that the barrier heights are more uncertain than usual.

Propyl system:

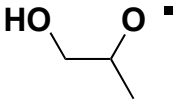
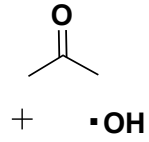
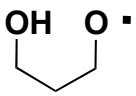
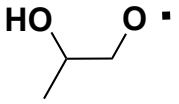
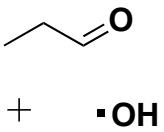
Energies for new OH and H transfer reaction pathways were calculated for propyl systems using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), CBS-CB3, and UCCSD(T)-F12/cc-pVT//M06-2X/6-311++G(d,p) levels of theory. Energies for transition states and products are listed in Table 3 and 4, respectively, relative to the lowest energy conformer.

Table 3. Transition state energies for propyl systems. Note that the H-transfer equivalent for pathway TS8 was not found.

		Relative energy[a]				
Species	Reaction	B3LYP[b]	M06-2X[b]	CBS-QB3	UCCSD(T)-F12	T1 diagnostic
TS4	$CH_3CH(CH_2)OOH \rightarrow CH_2(OH)CH(O)CH_3$	24.2	37.4	30.0	28.7[c]	0.066
TS4-2	$CH_3CH(CH_2)OOH \rightarrow (CH_3)_2CO + OH$	20.4	31.9	29.6	27.7[d]	0.065
TS8	$CH_2CH_2CH_2OOH \rightarrow CH_2(OH)CH_2CH_2O$	20.3	30.6	23.7	23.8[c]	0.069
TS9	$CH_3CHCH_2OOH \rightarrow CH_3CH(OH)CH_2O$	19.5	32.4	22.3	22.9[c]	0.094
TS9-22	$CH_3CHCH_2OOH \rightarrow CH_3CH_2CHO + OH$	15.7	27.7	26.5	23.7[c]	0.072

[a]All energies are relative to respective reactant in kcal/mol.
[b]Present work employing 6-311++G(d,p) basis set.
[c]Present work employing cc-pVTZ//M06-2X/6-311++G(d,p) basis set.
[d]Present work employing cc-pVDZ//M06-2X/6-311++G(d,p) basis set.

Table 4. Product energies of propyl systems.

Species	Structure	Relative energy[a]				T1 diagnostic
		B3LYP[b]	M06-2X[b]	CBS-QB3	UCCSD(T)-F12	
4product		-53.1	-53.9	-50.6	-51.2[d]	0.083
4-2product		-50.4	-46.8	-46.0	-47.4[c]	
8product		-52.3	-53.8	-50.3	-50.5[c]	0.069
9product		-52.8	-55.1	-52.1	-52.7[c]	0.094
9-22product		-42.2	-40.1	-39.7	-41.1[c]	

[a]All energies are relative to respective reactant in kcal/mol.
[b]Present work employing 6-311++G(d,p) basis set.
[c]Present work employing cc-pVTZ//M06-2X/6-311++G(d,p) basis set and geometry.
[d]Present work employing cc-pVDZ//M06-2X/6-311++G(d,p) basis set and geometry.
[e]Present work employing cc-pVQZ//M06-2X/6-311++G(d,p) basis set and geometry.

Similar to the ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems, the OH transfer reaction pathway was very exothermic and higher in energy than the H transfer pathway. The new reactions of species 4, 4-2, 8, 9, and 9-22 were also compared to the more common pathways (Figure 5 and 6).

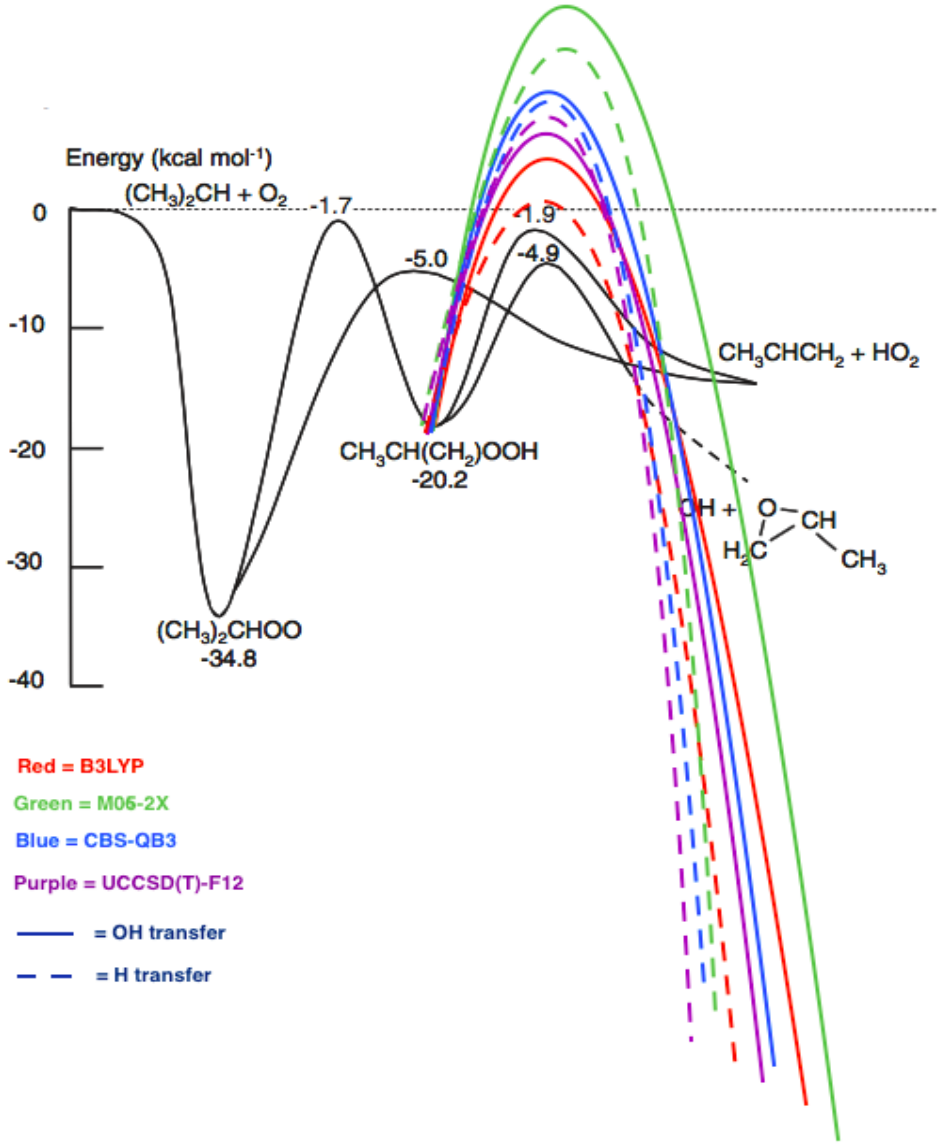


Figure 5. Schematic potential energy surfaces comparing calculated energy barriers of new OH transfer (4) and H transfer (4-2) pathways and those of common HO_2 and OH elimination pathways from $CH_3CH_2(CH_2)OOH$ using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), CBS-CB3, and UCCSD(T)-F12/cc-pVDZ//M06-2X/6-31++G(d,p) levels of theory. Drawn barriers represent E + ZPE values in kcal/mol relative to the i-propyl + O_2 entrance channels; lowest energy conformers from Goldsmith et al.[3] are used for reactants and relevant products.$TS4_{B3LYP}$= 4.0, $TS4_{M06\text{-}2x}$=17.2, $TS4_{CBS\text{-}QB3}$= 9.8, $TS4_{UCCSD(T)\text{-}F12}$= 6.5; $TS4\text{-}2_{B3LYP}$= 0.2, $TS4\text{-}2_{M06\text{-}2x}$=11.7, $TS4\text{-}2_{CBS\text{-}QB3}$= 9.4, $TS4\text{-}2_{UCCSD(T)\text{-}F12}$= 7.5. $4product_{B3LYP}$= -73.3,

4product$_{M06\text{-}2x}$= -74.1, 4product$_{CBS\text{-}QB3}$= -70.8, 4product$_{UCCSD(T)\text{-}F12}$= -71.4; 4-2product$_{B3LYP}$= -70.6, 4-2product$_{M06\text{-}2x}$= -67.0, 4-2product$_{CBS\text{-}QB3}$= -66.2, 4-2product$_{UCCSD(T)\text{-}F12}$= -67.9. Base figure adapted from Huang et al.[4]

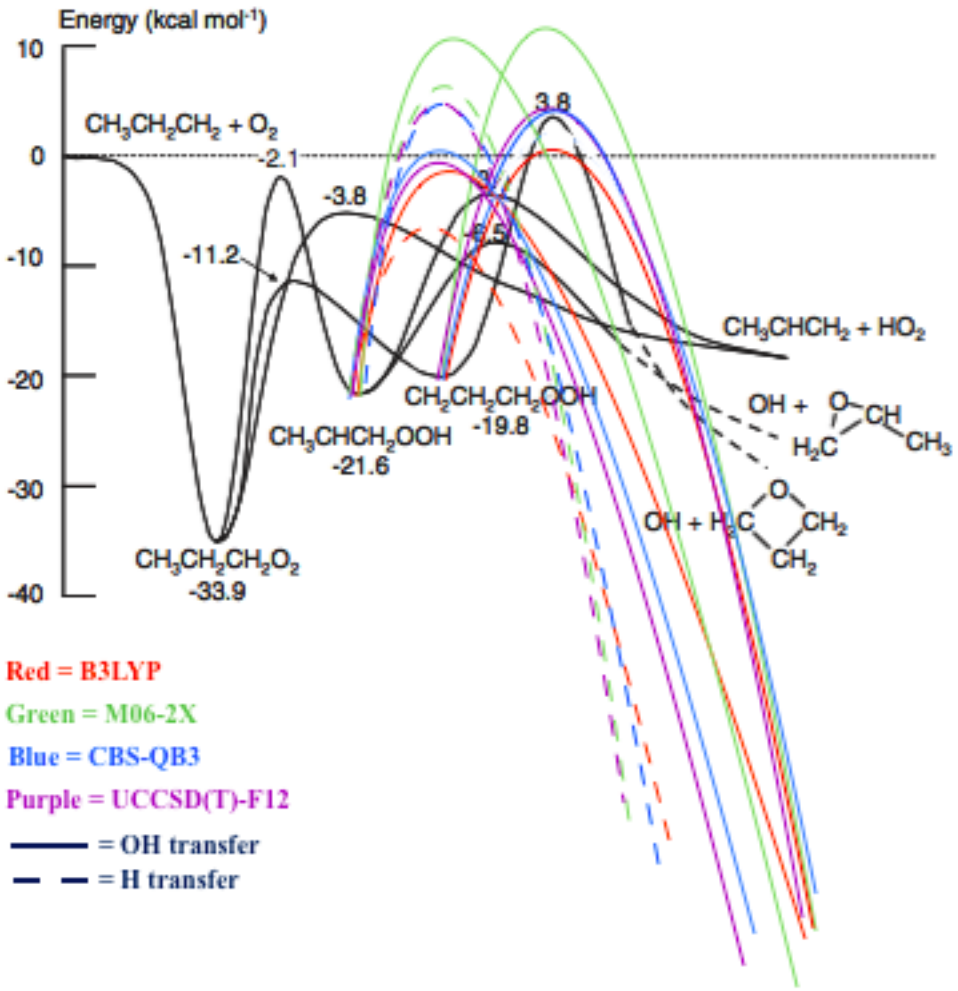


Figure 6. Schematic potential energy surfaces comparing calculated energy barriers of new OH transfer (8 and 9) and H transfer (9-22) pathways and those of common HO_2 and OH elimination pathways from $CH_2CH_2CH_2OOH$ (8) and CH_3CHCH_2OOH (9 and 9-22) using B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p), CBS-CB3, and UCCSD(T)-F12/cc-pVDZ//M06-2X/6-31++G(d,p) levels of theory. Drawn barriers represent E + ZPE values in kcal/mol relative to the n-propyl + O_2 entrance channels; lowest energy conformers from Goldsmith et al.[3] are used for reactants and relevant products. TS8$_{B3LYP}$= 0.5, TS8$_{M06\text{-}2x}$=10.8, TS8$_{CBS\text{-}QB3}$= 3.9, TS8$_{UCCSD(T)\text{-}F12}$= 4.0; TS9$_{B3LYP}$= -1.8, TS9$_{M06\text{-}2x}$=10.4, TS9$_{CBS\text{-}QB3}$= 0.5, TS9$_{UCCSD(T)\text{-}F12}$= -0.2; TS9-22$_{B3LYP}$= -5.6, TS9-22$_{M06\text{-}2x}$=5.6, TS9-22$_{CBS\text{-}QB3}$= 4.8, TS9-22$_{UCCSD(T)\text{-}F12}$= 4.8. 8product$_{B3LYP}$= -72.1, 8product$_{M06\text{-}2x}$= -73.6, 8product$_{CBS\text{-}QB3}$= -70.1, 8product$_{UCCSD(T)\text{-}F12}$= -70.3; 9product$_{B3LYP}$= -74.1, 9product$_{M06\text{-}2x}$= -77.2, 9product$_{CBS\text{-}QB3}$= -73.9, 9product$_{UCCSD(T)\text{-}F12}$= -75.9; 9-22product$_{B3LYP}$= -63.6, 9-22product$_{M06\text{-}2x}$= -62.2, 9-22product$_{CBS\text{-}QB3}$= -66.0, 9-22product$_{UCCSD(T)\text{-}F12}$= -60.0. Base figure adapted from Huang et al.[4]

While the OH transfer and H transfer reaction pathway for the i-propyl system (4 and 4-2) and 9 and 9-22 were high in energy, the OH transfer for 8 revealed considerable comparison with the cyclic ether formation—while the cyclic ether formation undergoes a 4-membered ring transition state, the OH transfer undergoes a 5-membered ring transition state, which is much more favorable in energy. Though the H transfer was higher in energy than most OH transfer reactions, a H transfer transition structure could not be found for species 8. Several slight changes in transition state conformations for each species and reaction type often lead to very different reactions, highlighting the uniqueness of these two new reaction pathways.

References

(1) Burke, M.P.; Goldsmith, C.F.; Klippenstein, S.J.; Welz, O.; Huang, H.; Antonov, I.O.; Savee, J.D.; Osborn, D.L.; Zádor, J.; Taatjes, C.A.; Sheps, L. Multiscale informatics for low-temperature propane oxidation: Further complexities in studies of complex reactions. *J. Phys. Chem. A* **2015,** 119, 7095-7115.

(2) DeSain, J. D.; Klippenstein, S.J.; Miller, J.A.; Taatjes, C.A.; Measurements, Theory, and Modeling of OH formation in Ethyl + O_2 and Propyl + O_2 Reactions. *J. Phys. Chem. A* **2003**, 107, 4415-4427.

(3) Goldsmith, C.F.; Green, W.H.; Klippenstein, S.J. Role of O_2 + QOOH in low-temperature ignition of propane. 1. Temperature and pressure dependent rate coefficients. *J. Phys. Chem. A* **2012**, 116, 3325-3346.

(4) Huang, H.; Merthe, D.J.; Zádor, J.; Jusinski, L.E.; Taatjes, C.A. New experiments and validated master-equation modeling for OH production in propyl + O_2 reactions. *Proc. Combust. Inst*. 33 **2011**, 293-299.

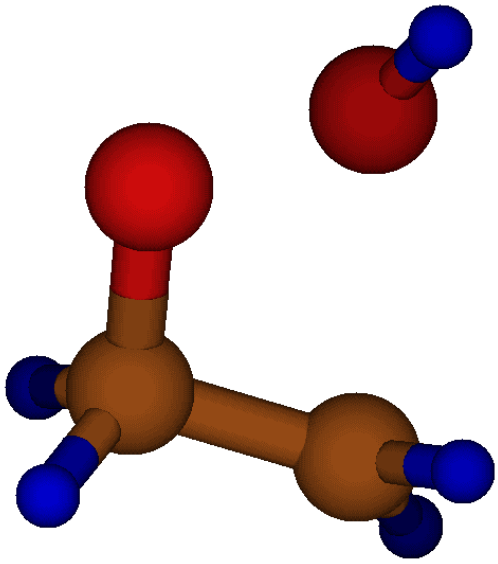
(5) Knepp, A.M.; Meloni, G.; Jusinski, L.E.; Taatjes, C.A.; Cavallotti, C.; Klippenstein, S. J. Theory, measurements, and modeling of OH and HO_2 formation in the reaction of cyclohexyl radicals with O_2. *Phys. Chem. Chem. Phys*. **2007**, 9, 4315-4331.

(6) Miller, J.A.; Klippenstein, S.J.; Roberston, S.H. A theoretical analysis of the reaction between ethyl and molecular oxygen. *Proc. Combust. Inst***. 2000**, 28, 1479-1486.

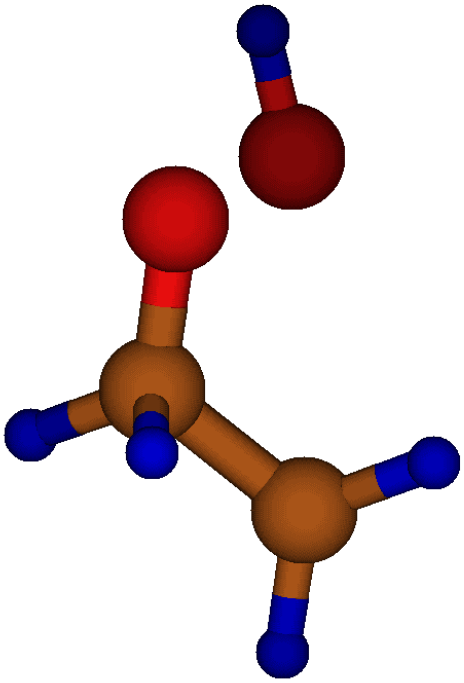
(7) Zádor, J.; Fernandes, R.X.; Georgievskii, Y.; Meloni, G.; Taatjes, C.A.; Miller, J.A. The reaction of hydroxyethyl radical with O_2: A theoretical analysis and experimental study. *Proc. Combust. Inst.* **2009**, 32, 271-277.

(8) Manley, D.K.; McIlroy, A.; Taatjes, C.A. Research needs for future internal combustion engines. *Physics Today, Scientific American* **2008**, Nov., 47-52.

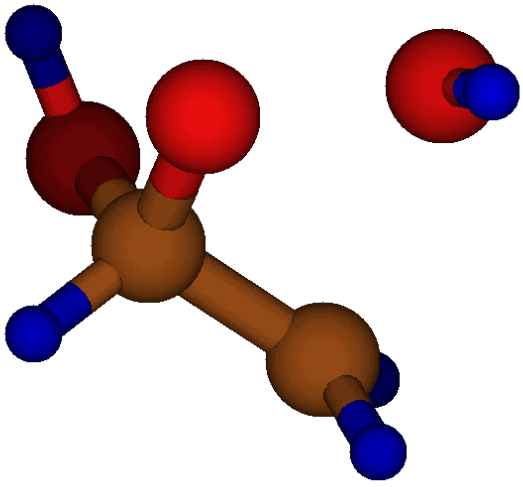
Appendix A: Images of M06-2x/6-311++G(d,p) optimized transition states of ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems.



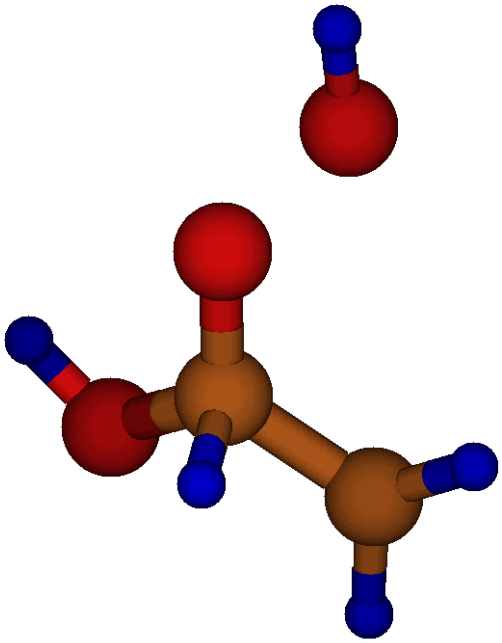
TS1



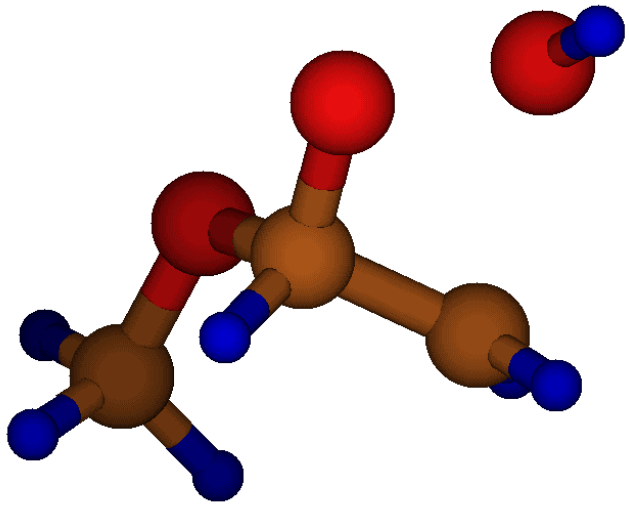
TS1-2



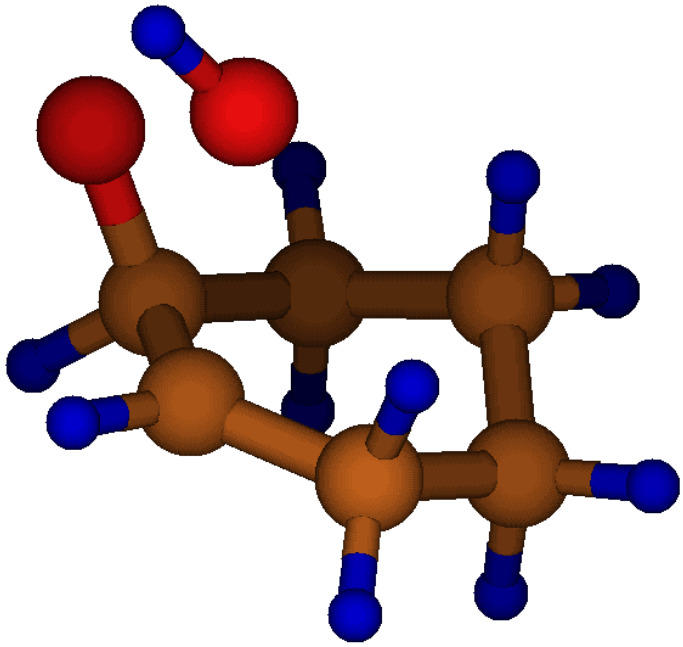
TS2



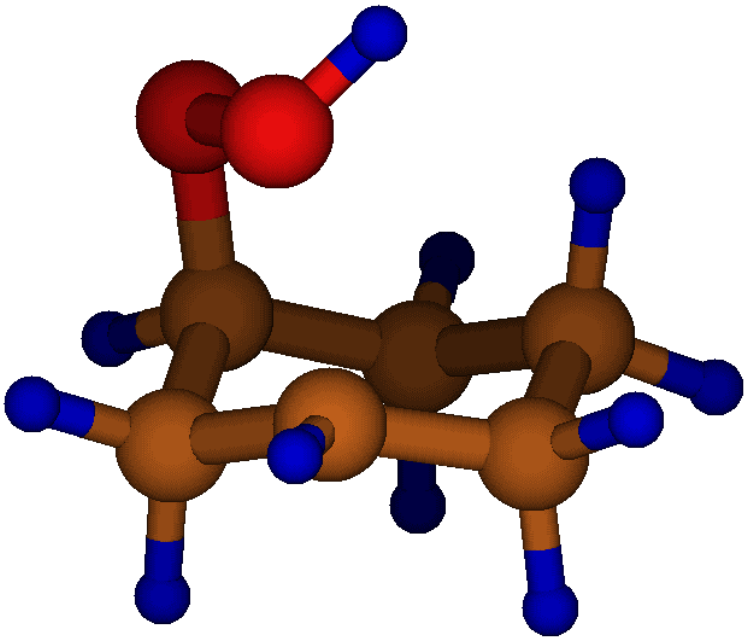
TS2



TS3

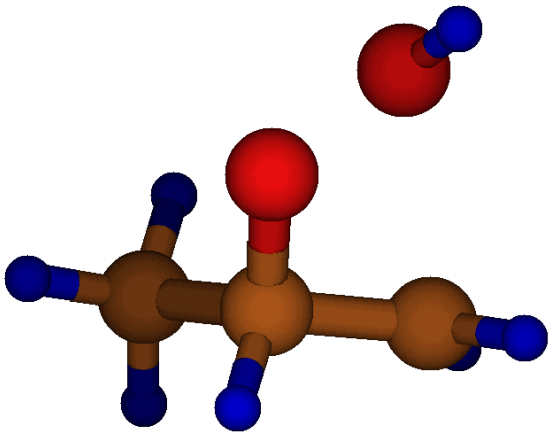


TS5

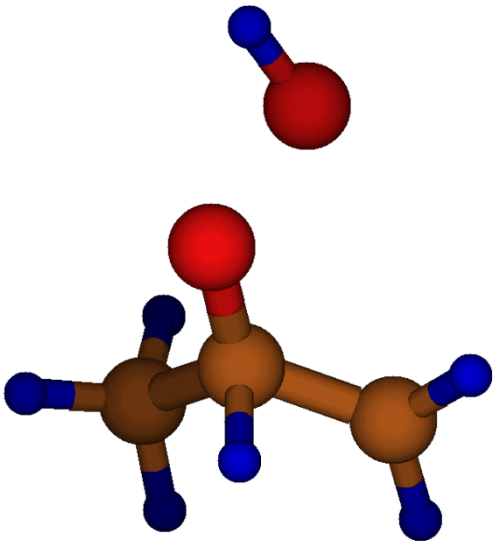


TS6

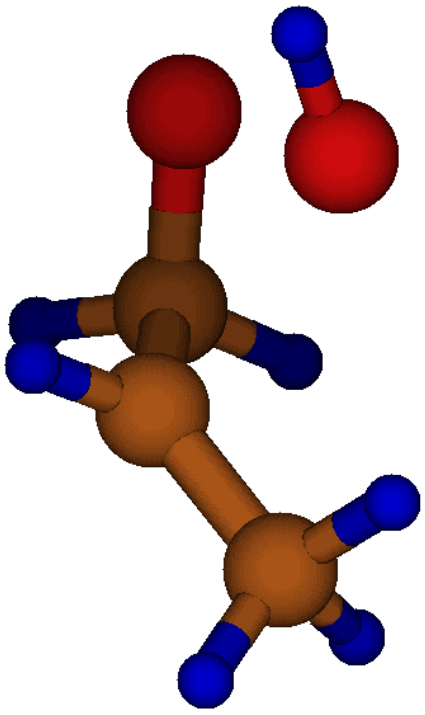
Appendix B: Images of M06-2x/6-311++G(d,p) optimized transition states of propyl systems.



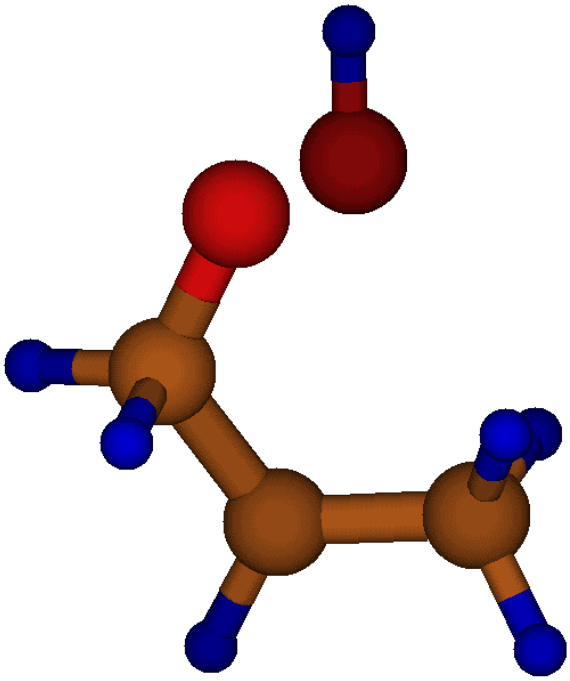
TS4



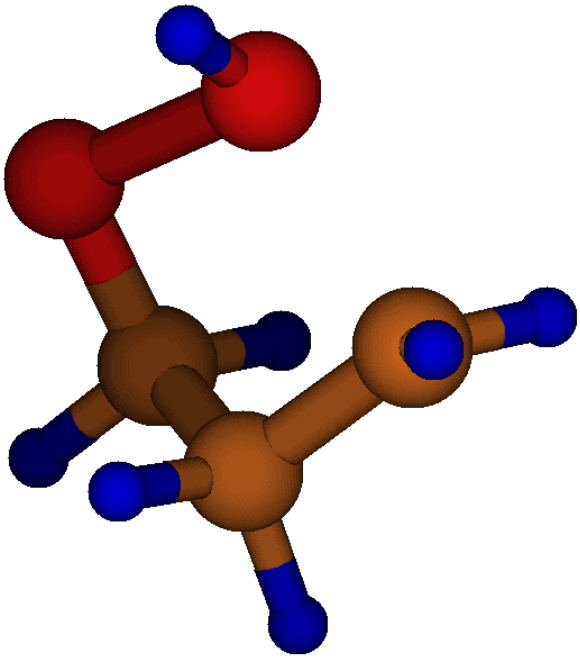
TS4-2



TS9



TS9-22



TS8

Appendix C: M06-2x/6-311++G(d,p) optimized geometries of ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems in Cartesian coordinates (Angstroms).

1reactant

C	-0.057625	0.180951	-0.128217
H	-0.185634	0.227242	0.959785
O	1.355906	0.041011	-0.262939
C	-0.804693	-0.957915	-0.721825
H	-0.364654	1.137158	-0.558409
H	-1.600003	-0.804143	-1.436466
H	-0.565277	-1.968256	-0.415418
O	1.667752	0.196643	-1.640961
H	1.816194	-0.715284	-1.921199

TS1

C	1.046292	-1.351071	-0.176859
C	-0.000973	-0.482963	0.382785
O	1.615829	0.901455	0.040841
O	1.743991	-0.516743	-1.042293
H	1.482135	1.476670	-0.722373
H	-0.711564	-0.035136	-0.299709
H	0.628393	-2.165858	-0.788292
H	1.684005	-1.777375	0.605132
H	-0.221740	-0.449998	1.441372

1product

C	0.034240	-0.003771	-0.010058
H	0.116041	-0.028324	1.089149
O	1.294686	0.128826	-0.528662
C	-0.723760	-1.220331	-0.503577
H	-0.511452	0.926961	-0.241337
H	-0.644061	-1.264201	-1.595425
O	-0.134416	-2.352376	0.105894
H	-1.782528	-1.130137	-0.228122
H	-0.413065	-3.146496	-0.353525

1-2reactant

H	1.245160	-0.716359	-0.708317
C	0.835123	-0.371067	0.245632
C	1.156848	1.055569	0.495537
O	-0.563657	-0.632939	0.288297
O	-1.151071	0.101362	-0.786116
H	-1.649727	-0.595578	-1.228453
H	1.213558	-1.021618	1.044481
H	1.834530	1.600877	-0.144298
H	0.678302	1.568174	1.318700

TS1-2

H	1.003490	-1.551255	0.344618
C	0.352693	-1.042559	1.066689
C	0.679308	0.343877	1.336316
O	-0.864015	-1.482622	1.224911
O	-1.762677	-0.503698	-0.064952
H	-2.505110	-1.121974	-0.049637
H	0.851730	-1.143101	2.117405
H	1.692093	0.694397	1.186210
H	-0.027541	0.941231	1.897792

1-2product

H	1.906549	-1.178359	0.383968
C	0.996071	-0.581079	0.189505
C	1.124549	0.897312	0.394776
O	-0.011680	-1.139926	-0.164092
O	-2.030377	0.818386	-0.500682
H	-1.609610	-0.064987	-0.488661
H	1.428646	1.088173	1.427675
H	1.922755	1.278674	-0.247934
H	0.190158	1.414810	0.178470

2reactant

C	-0.081813	0.111220	-0.102511
C	-0.133482	0.226228	1.372283
O	1.244842	0.051680	-0.518313
O	-0.786479	-1.084023	-0.427559
H	-0.611038	0.932028	-0.606034
O	-0.843766	-1.121527	-1.857829
H	-0.533198	-2.018782	-2.026911
H	1.251292	0.068271	-1.480178
H	-1.081879	0.383044	1.862892
H	0.762356	0.027684	1.941167

TS2

C	1.000284	-1.396125	-0.220933
C	0.006365	-0.499232	0.393733
O	1.682048	0.833507	0.045794
O	1.764587	-0.588292	-1.021338
H	1.543180	1.406992	-0.718448
H	-0.728829	-0.032010	-0.247034
H	0.529612	-2.130899	-0.900260

O	1.725389	-2.051943	0.785611
H	-0.147137	-0.512274	1.463997
H	2.629661	-2.135682	0.468264

2product

C	0.000219	-0.066415	-0.183757
H	0.201190	-0.014964	0.906448
O	1.183508	-0.365508	-0.891938
C	-0.950194	-1.276115	-0.410113
O	-0.575190	1.087393	-0.517061
O	-1.165367	-1.497004	-1.771256
H	-0.481234	-2.137757	0.077788
H	-1.909358	-1.061192	0.057515
H	-0.301289	-1.572304	-2.190802
H	1.600157	0.464973	-1.141146

2-2reactant

O	1.274239	-0.652640	-0.519327
C	0.501162	-0.157159	0.524350
C	0.700013	1.310178	0.603841
O	-0.869158	-0.532918	0.384819
O	-1.404106	0.085180	-0.779272
H	-1.975392	0.761805	-0.395320
H	0.733740	-0.650564	1.479257
H	1.163283	1.829989	-0.221013
H	0.329730	1.851931	1.462369
H	1.062745	-1.584096	-0.636215

TS2-2

O	1.022773	-1.491222	0.394236
C	0.180510	-0.878230	1.294139
C	0.511406	0.509892	1.553535
O	-1.030931	-1.330457	1.411756
O	-1.904770	-0.492658	0.063263
H	-2.746527	-0.903721	0.300695
H	0.564043	-0.989508	2.405954
H	1.530291	0.838719	1.406283
H	-0.184362	1.086054	2.145778
H	0.613475	-2.331907	0.163011

2-2product

O	1.745869	-0.934564	0.146206
C	0.584353	-0.270426	0.076765

C	0.701455	1.129462	0.598673
O	-0.415182	-0.784542	-0.360894
O	-2.505874	1.113911	-0.222457
H	-2.029080	0.277121	-0.397699
H	0.999320	1.094866	1.647632
H	1.482593	1.655628	0.048860
H	-0.248038	1.650106	0.496583
H	1.597252	-1.825172	-0.200668

3reactant

C	0.302419	0.199345	-0.382072
C	-0.370588	0.169306	0.942748
O	1.655406	0.494906	-0.148238
O	0.268693	-1.051568	-1.027676
H	-0.117319	0.966216	-1.048705
O	2.279603	0.686637	-1.410139
H	2.389803	-0.225169	-1.715566
C	-0.969273	-1.321509	-1.652090
H	-0.877302	-2.291876	-2.135735
H	-1.783739	-1.360856	-0.920218
H	-1.201890	-0.560890	-2.406597
H	-0.796661	1.069727	1.360290
H	-0.253047	-0.711417	1.559015

TS3

O	1.179292	-1.326720	-0.154280
H	0.350988	-0.834513	-0.216039
O	2.093440	0.183903	-0.239667
C	3.037607	-0.268943	-1.117656
H	3.376751	0.608284	-1.702006
C	2.309647	-1.253517	-1.952208
H	1.555168	-0.894813	-2.639384
O	4.127694	-0.836798	-0.441653
C	5.259755	-0.998879	-1.263182
H	6.050246	-1.413077	-0.640482
H	5.069095	-1.687686	-2.096412
H	5.592705	-0.036913	-1.673963
H	2.683856	-2.261902	-2.069096

3product

C	-0.082989	0.137308	-0.172126
H	-0.005167	0.033770	0.926142
O	1.043296	0.426128	-0.742291
O	-0.824927	-0.943344	-0.653010

C	-1.009344	1.463444	-0.335480
C	-0.462804	-1.386521	-1.949062
H	-1.191899	-2.145530	-2.223712
H	-0.493120	-0.565840	-2.673790
H	0.543456	-1.810566	-1.954416
H	-1.181342	1.563430	-1.411174
H	-1.937523	1.246239	0.188263
O	-0.404506	2.559558	0.244931
H	0.456084	2.685462	-0.169271

5reactant

C	1.038201	-1.346619	-0.282303
C	-0.876010	0.024589	0.750823
C	0.096712	1.153083	0.845275
C	1.431511	1.097770	0.178482
C	2.041817	-0.308479	0.218671
H	1.488536	-2.342595	-0.268126
H	0.765571	-1.124622	-1.316723
H	-1.362133	1.272368	-1.765296
H	-0.274299	2.101390	1.218729
H	1.320566	1.392010	-0.878073
H	2.108329	1.828399	0.630236
H	2.953966	-0.331956	-0.382385
H	2.327621	-0.547482	1.249611
H	-1.525442	0.015746	1.632764
O	-1.869501	0.262312	-0.271732
O	-1.212001	0.347973	-1.533988
C	-0.214886	-1.348031	0.597513
H	0.067054	-1.687644	1.600869
H	-0.965903	-2.045367	0.218972

TS5

C	1.029281	-1.408975	-0.229274
C	-0.894865	-0.078451	0.782570
C	-0.027415	1.099567	0.547766
C	1.398219	1.048636	0.171876
C	2.025073	-0.347154	0.238949
H	1.506259	-2.391702	-0.243045
H	0.694951	-1.182553	-1.245539
H	-1.637419	1.161157	-1.845535
H	-0.495064	2.066928	0.692939
H	1.383146	1.389373	-0.880992
H	1.981861	1.793529	0.722266
H	2.932390	-0.362003	-0.368204
H	2.326927	-0.567324	1.268902

H	-1.400825	0.034699	1.756108
O	-1.915915	0.069906	-0.162474
O	-0.866017	0.721321	-1.470533
C	-0.174316	-1.429397	0.713475
H	0.167399	-1.703950	1.718382
H	-0.912013	-2.171684	0.403303

5product

C	1.079973	-1.396739	-0.205939
C	-0.778799	0.016575	0.861563
C	-0.199223	1.077217	-0.081868
C	1.330792	1.100553	-0.002970
C	1.931663	-0.265792	0.368115
H	1.559449	-2.364523	-0.041863
H	0.979932	-1.253382	-1.283597
H	-1.542727	0.671792	-1.414819
H	-0.602573	2.054018	0.211252
H	1.688199	1.418307	-0.985319
H	1.647404	1.859341	0.716208
H	2.956916	-0.332112	-0.000771
H	1.985055	-0.373307	1.457333
H	-0.439928	0.197747	1.892457
O	-2.142418	-0.032486	0.798056
O	-0.585966	0.788875	-1.414747
C	-0.316707	-1.422670	0.436505
H	-0.335893	-2.044600	1.332498
H	-1.049206	-1.829750	-0.262028

6reactant

C	0.842345	-0.660718	-0.453821
C	-0.521339	-0.827277	-1.131978
C	-1.625422	0.108351	-0.623975
C	-1.143333	1.573564	-0.617672
C	0.142100	1.693846	0.129887
C	1.259790	0.817787	-0.327163
O	0.958713	-1.358544	0.782595
O	0.106175	-0.741687	1.749578
H	-2.505714	0.007720	-1.265561
H	-1.922544	-0.170316	0.388071
H	-0.400093	-1.503414	2.055298
H	2.130294	0.879968	0.327854
H	0.175622	2.156151	1.106383
H	-1.912683	2.224659	-0.199126
H	-0.991712	1.883595	-1.663265
H	1.596589	-1.193533	-1.042013

H	1.581714	1.132281	-1.331873
H	-0.366704	-0.629017	-2.199730
H	-0.825089	-1.874734	-1.048304

TS6

C	2.452924	-1.396908	0.547380
C	1.155298	-1.444913	-0.264846
C	0.010891	-0.659391	0.381235
C	0.433558	0.772418	0.748353
C	1.758925	0.819863	1.436992
C	2.887045	0.054598	0.797191
O	2.350533	-2.092384	1.782582
O	1.739451	-0.832193	2.702213
H	-0.843619	-0.623844	-0.298984
H	-0.327992	-1.183159	1.277976
H	0.921650	-1.197559	3.081421
H	3.769463	0.061451	1.438563
H	2.005506	1.687717	2.037812
H	-0.336191	1.265471	1.346162
H	0.520360	1.353998	-0.185024
H	3.238140	-1.930436	-0.003976
H	3.163068	0.520564	-0.160372
H	1.364856	-1.031839	-1.259228
H	0.864784	-2.489099	-0.403168

6product

C	0.882951	-0.868858	-0.710757
C	-0.427496	-0.785401	-1.506182
C	-1.546786	-0.149629	-0.682940
C	-1.143483	1.242606	-0.194916
C	0.153250	1.206839	0.617938
C	1.283926	0.544062	-0.169861
O	0.762739	-1.653535	0.404745
O	-0.030780	0.596996	1.882197
H	-2.459099	-0.088675	-1.280208
H	-1.778305	-0.792079	0.172162
H	-0.125805	-0.354757	1.756437
H	2.173044	0.452767	0.455720
H	0.458483	2.232347	0.844184
H	-1.928402	1.678899	0.426366
H	-0.998429	1.903488	-1.057965
H	1.712798	-1.222429	-1.339043
H	1.536268	1.143622	-1.049766
H	-0.235497	-0.192189	-2.407844
H	-0.704098	-1.790505	-1.833439

Appendix D: M06-2X/6-311++G(d,p) optimized geometries of propyl systems in Cartesian coordinates (Angstroms).

9reactant/9-22reactant

O	0.009985	-0.313206	-0.674872
H	-0.074107	0.467856	-0.115496
O	1.415911	-0.336488	-0.916703
C	1.908268	-1.574347	-0.385403
H	1.312859	-2.384519	-0.823760
H	1.778253	-1.579678	0.700555
C	3.334150	-1.675817	-0.784227
H	4.099167	-1.433092	-0.057884
C	3.698171	-1.824565	-2.219048
H	4.695954	-2.249666	-2.341013
H	2.977378	-2.460351	-2.740885
H	3.688507	-0.853773	-2.732051

TS9

H	1.055929	-1.398718	-0.155759
O	0.369301	-0.875736	0.273809
O	1.313101	0.617335	-0.064542
C	0.729292	1.326137	0.974294
H	1.413165	2.154706	1.217638
C	0.627074	0.368907	2.089495
H	1.556803	-0.088131	2.409487
H	-1.000408	-0.872073	2.349988
H	-0.467618	-0.129244	3.870277
C	-0.619007	0.057625	2.806257
H	-1.380815	0.825052	2.662330
H	-0.254331	1.736280	0.711170

9product

H	-0.147340	-0.874184	-1.475452
O	-0.761749	-0.913776	-0.734238
O	1.328180	0.885181	-1.084407
C	0.531082	0.963248	0.025264
H	1.058438	1.435264	0.866822
C	-0.101438	-0.381308	0.393585
H	0.704531	-1.057552	0.711146
H	-0.651092	0.179188	2.406839
H	-1.924722	0.429299	1.189688
C	-1.116191	-0.232640	1.508549
H	-1.545742	-1.204229	1.753055

H	-0.281603	1.655904	-0.271975

TS9-22

O	0.441203	-1.041042	-1.583935
H	-0.181295	-0.307191	-1.506157
O	1.623451	-0.147899	-0.378662
C	2.258026	-1.205313	0.082474
H	1.771526	-1.770937	0.892846
H	3.221266	-0.808290	0.551170
C	3.008572	-2.044735	-0.836403
H	3.454196	-2.950151	-0.435789
C	3.294961	-1.588938	-2.203288
H	4.161612	-2.073904	-2.648093
H	2.397701	-1.780793	-2.810125
H	3.393275	-0.498454	-2.214824

9-22product1

O	-2.084821	-0.018006	-0.945809
C	-2.018836	1.040461	-0.382450
H	-1.152626	1.271772	0.270545
C	-3.056521	2.127083	-0.491630
H	-3.387514	2.356952	0.528376
H	-2.538780	3.030435	-0.836183
C	-4.221818	1.759472	-1.397776
H	-3.870681	1.543945	-2.407547
H	-4.726222	0.864546	-1.031616
H	-4.946113	2.573096	-1.446382

OH

O	-2.007932	-0.022230	-0.953107
H	-2.007092	0.830003	-0.485636

8reactant

O	0.028575	0.000122	-0.038476
H	-0.006319	0.054084	0.923756
O	1.437616	0.000717	-0.260034
C	1.723225	1.093306	-1.114091
H	2.815338	1.119362	-1.143605
H	1.358018	2.021386	-0.659389
C	1.145187	0.911146	-2.514159
H	1.547873	-0.006600	-2.949604
H	0.061402	0.761489	-2.409051
C	1.435189	2.086439	-3.379988

H	1.301071	3.090974	-2.998004
H	1.630641	1.970845	-4.436228

TS8

C	0.998336	-1.348445	-0.324618
C	-0.175611	-0.699323	0.411039
O	1.909077	0.652354	0.277422
O	1.745101	-0.373230	-1.019921
H	1.736297	1.493326	-0.174326
H	0.659687	-2.067158	-1.079510
H	1.639955	-1.877060	0.392236
H	-0.809086	-1.485989	0.843367
C	0.314567	0.231050	1.486992
H	-0.785719	-0.154102	-0.314130
H	-0.266795	1.112566	1.730885
H	0.919029	-0.178605	2.285898

8product

C	-0.016356	-1.331103	-0.496794
C	-0.997745	-0.596549	0.414391
O	-0.227490	1.542501	-0.234088
O	1.151046	-1.690673	0.118175
H	0.257535	2.329136	0.022357
H	0.297846	-0.649190	-1.310831
H	-0.469792	-2.199371	-0.997054
H	-1.244989	-1.233196	1.268064
C	-0.416258	0.714226	0.906712
H	-1.921751	-0.397432	-0.136214
H	-1.100112	1.187629	1.619479
H	0.538039	0.521588	1.409339

4reactant/4-22reactant

C	0.004028	-0.023998	-0.069557
H	0.214168	0.870991	0.504486
H	0.717230	-0.835456	-0.054749
C	-1.270260	-0.106671	-0.837162
H	-1.336675	-1.058302	-1.372209
C	-2.497955	0.100961	0.041079
H	-3.404268	0.074186	-0.565234
H	-2.548881	-0.684365	0.796347
H	-2.438205	1.067317	0.545759
O	-1.358038	0.945872	-1.809474
O	-0.368967	0.711194	-2.800358
H	0.334488	1.317487	-2.535550

TS4

O	1.202831	-1.314895	-0.108923
H	0.352994	-0.859710	-0.145024
O	2.047423	0.250047	-0.328251
C	3.021907	-0.282269	-1.172093
H	3.364967	0.564818	-1.790990
C	2.261494	-1.241339	-1.994520
H	1.440757	-0.869882	-2.593908
C	4.181972	-0.909901	-0.413053
H	2.624519	-2.243010	-2.189269
H	4.928031	-1.317647	-1.099540
H	4.657087	-0.160585	0.220129
H	3.800761	-1.710640	0.222919

4product

O	-1.159283	-1.148048	0.267028
H	-1.506951	-0.417125	0.789511
O	-0.084556	1.439043	0.327403
C	0.505167	0.468880	-0.447935
H	0.976038	0.920628	-1.333220
C	-0.526386	-0.588014	-0.857991
H	-1.256953	-0.127771	-1.534272
C	1.617249	-0.135567	0.437898
H	-0.031149	-1.401536	-1.392336
H	2.161675	-0.870583	-0.157091
H	2.304793	0.641382	0.768955
H	1.174022	-0.630868	1.300539

TS4-2

O	1.788253	-0.106745	-0.436950
C	2.936490	-0.441211	-0.971968
C	2.936085	-1.023590	-2.304472
C	4.071426	-0.793884	-0.031629
O	1.034254	-1.738469	-0.165266
H	3.871671	-1.295266	-2.775437
H	2.029723	-0.955084	-2.891653
H	3.189141	0.481097	-1.655912
H	4.164881	-0.029966	0.738999
H	3.807910	-1.740954	0.442573
H	5.021653	-0.907306	-0.555303
H	0.411004	-1.380907	0.480034

4-2product1

H	-1.713198	-1.129448	1.236811
H	-2.210525	0.574333	1.458159
C	-1.474395	-0.088119	1.007731
H	-1.501606	0.017767	-0.080227
H	0.873864	-1.653502	1.505820
C	-0.090647	0.258396	1.512594
C	1.031057	-0.659554	1.078071
H	1.030936	-0.772256	-0.008754
H	1.986671	-0.263372	1.414905
O	0.107050	1.212677	2.221518

Appendix E: M06-2x/6-311++G(d,p) frequencies of ethane, ethanol, ethyl methyl ether, and cyclohexane radical systems (cm^{-1}).

1reactant

Frequencies --	134.3884	180.8361	195.3431
Frequencies --	368.6969	460.8797	577.2108
Frequencies --	835.4136	923.5550	1036.5740
Frequencies --	1095.6598	1158.8520	1298.4736
Frequencies --	1383.4176	1399.2603	1458.8713
Frequencies --	1478.6609	3050.9221	3112.2493
Frequencies --	3175.5225	3289.7020	3837.6513

TS1

Frequencies --	-2692.5586	219.8235	380.4119
Frequencies --	401.8513	522.6151	567.8120
Frequencies --	800.1372	897.9513	967.4354
Frequencies --	1023.6982	1079.2689	1176.8579
Frequencies --	1189.8525	1348.9769	1465.8124
Frequencies --	1491.2997	3013.2133	3070.8073
Frequencies --	3172.2589	3290.2523	3875.2597

1product

Frequencies --	151.0160	229.1646	330.1338
Frequencies --	441.3968	602.3490	899.2497
Frequencies --	998.3926	1092.7105	1110.0191
Frequencies --	1165.3803	1273.2958	1291.2220
Frequencies --	1370.5950	1400.7403	1458.4927
Frequencies --	1511.3812	2975.6414	3007.4826
Frequencies --	3027.1359	3078.0110	3925.6365

1-2reactant

Frequencies --	76.0708	164.3557	174.9088
Frequencies --	366.8620	440.9606	555.1638
Frequencies --	843.5011	920.8022	1034.2229
Frequencies --	1108.8939	1149.7451	1292.9017
Frequencies --	1381.1032	1411.4625	1459.2177
Frequencies --	1476.4598	3037.0199	3090.7942

```
 Frequencies --  3185.4656              3300.1934              3859.1753


TS1-2
 Frequencies -- -1429.9086               123.1217               169.2146
 Frequencies --   232.5445               279.2340               477.9464
 Frequencies --   559.1713               768.3719               853.0946
 Frequencies --   959.0765               969.2477              1157.6176
 Frequencies --  1242.3405              1319.7683              1411.7247
 Frequencies --  1492.6939              2512.2235              3051.8014
 Frequencies --  3175.8505              3302.9597              3862.2768


1-2product
 Frequencies --    43.8601                79.1542               139.8010
 Frequencies --   193.1655               382.1823               434.8174
 Frequencies --   529.5616               780.0241               904.6960
 Frequencies --  1144.5814              1145.9263              1388.3519
 Frequencies --  1432.2515              1464.3556              1469.0866
 Frequencies --  1853.8687              2977.8433              3060.5426
 Frequencies --  3129.7968              3168.6101              3672.7566


2reactant
 Frequencies --   134.5453               163.9720               205.2613
 Frequencies --   290.0180               381.4138               443.3031
 Frequencies --   475.6743               568.3200               615.7175
 Frequencies --   916.8501               970.2709              1028.3587
 Frequencies --  1082.8369              1183.4240              1273.3097
 Frequencies --  1358.7953              1413.6518              1421.7053
 Frequencies --  1494.9797              3027.9471              3199.4478
 Frequencies --  3323.1134              3864.1577              3889.0325


TS2
 Frequencies -- -2739.4163                91.2877               171.5683
 Frequencies --   385.6128               407.7106               425.7622
 Frequencies --   514.5046               520.4302               686.8628
 Frequencies --   865.1141               922.5557               988.6767
 Frequencies --  1025.6875              1088.8946              1158.0275
 Frequencies --  1203.7679              1322.3115              1368.0104
 Frequencies --  1474.2943              2969.8397              3181.9752
 Frequencies --  3309.9954              3869.1027              3894.1564


2product
 Frequencies --   131.9682               241.0974               260.9302
 Frequencies --   369.6104               440.2605               529.4257
 Frequencies --   652.3762               798.6393               878.2748
 Frequencies --   995.6712              1065.7187              1145.7089
 Frequencies --  1182.6856              1224.1214              1286.3943
 Frequencies --  1315.0659              1387.6192              1418.4825
 Frequencies --  1503.1239              2903.6336              3056.2500
 Frequencies --  3164.7452              3865.6778              3891.9488


2-2reactant
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 Frequencies --   147.4682              166.4723              184.0060
 Frequencies --   288.3444              339.8698              409.4306
 Frequencies --   456.5743              515.1630              749.6285
 Frequencies --   887.4336              929.2265             1033.9713
 Frequencies --  1081.8156             1189.1685             1276.4692
 Frequencies --  1375.1376             1402.6038             1414.0565
 Frequencies --  1478.4199             3027.5749             3191.5819
 Frequencies --  3314.4318             3843.6124             3884.9280


TS2-2
 Frequencies -- -1492.5425               85.0638              155.9554
 Frequencies --   181.7564              287.0215              355.2472
 Frequencies --   426.3809              499.8224              545.3628
 Frequencies --   710.4290              790.9762              917.6866
 Frequencies --   937.5134             1001.7026             1128.9908
 Frequencies --  1202.7931             1348.7117             1412.6504
 Frequencies --  1508.6656             2383.2276             3196.3594
 Frequencies --  3327.1368             3861.6947             3881.6409


2-2product
 Frequencies --    24.7980               53.9114               91.7252
 Frequencies --   182.7856              419.9848              428.6693
 Frequencies --   442.6472              550.8454              613.1925
 Frequencies --   674.7585              895.0223             1023.2164
 Frequencies --  1074.5118             1248.5329             1365.8475
 Frequencies --  1436.4406             1471.1347             1480.5459
 Frequencies --  1852.8107             3086.9966             3161.4090
 Frequencies --  3192.4338             3664.4589             3825.7430


3reactant
 Frequencies --    90.6404              154.7992              185.5531
 Frequencies --   204.2937              277.0237              304.4426
 Frequencies --   395.3079              415.0083              527.8332
 Frequencies --   587.2433              606.0466              872.4493
 Frequencies --  1003.3325             1084.8679             1112.4426
 Frequencies --  1143.7540             1174.3760             1189.1739
 Frequencies --  1246.4165             1361.0424             1397.6657
 Frequencies --  1426.6546             1458.2707             1489.3118
 Frequencies --  1502.1302             1518.2655             3024.3236
 Frequencies --  3030.6338             3086.4904             3168.8219
 Frequencies --  3184.6472             3304.6123             3807.3817


TS3
 Frequencies -- -3353.5410              106.8077              140.4692
 Frequencies --   203.1877              317.4333              379.0618
 Frequencies --   421.0181              443.4890              510.2739
 Frequencies --   541.2179              705.8511              849.1668
 Frequencies --   894.6562             1008.9616             1043.3849
 Frequencies --  1079.7254             1145.0910             1177.5561
 Frequencies --  1187.7295             1214.7647             1263.1317
 Frequencies --  1371.7984             1463.5068             1488.1043
 Frequencies --  1503.1902             1516.2168             2951.5386
 Frequencies --  3011.5112             3062.5748             3164.2113
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 Frequencies --  3175.8131              3299.8442              3867.2911


3product
 Frequencies --    84.9368               151.9196               193.8173
 Frequencies --   247.4069               325.5466               372.4008
 Frequencies --   416.7327               467.5985               548.3928
 Frequencies --   704.1092               907.5440               972.6793
 Frequencies --  1050.3257              1150.4763              1169.5226
 Frequencies --  1183.7598              1196.9351              1215.4331
 Frequencies --  1259.6603              1300.7406              1365.5317
 Frequencies --  1408.5971              1482.6300              1494.7488
 Frequencies --  1511.1985              1515.5882              2939.9416
 Frequencies --  3046.2748              3072.7490              3115.0399
 Frequencies --  3175.8101              3178.7477              3867.4445


5reactant
 Frequencies --    93.9635               138.1567               180.8401
 Frequencies --   201.2285               262.1757               324.1889
 Frequencies --   389.9435               421.4351               458.1070
 Frequencies --   478.7687               612.4818               728.5223
 Frequencies --   765.1765               833.3155               864.8330
 Frequencies --   894.4354               916.6683               929.1824
 Frequencies --  1006.3496              1040.3655              1066.6022
 Frequencies --  1078.2597              1091.9434              1139.2490
 Frequencies --  1168.5446              1198.7817              1276.0736
 Frequencies --  1304.3925              1343.0388              1353.5302
 Frequencies --  1366.3956              1376.9542              1390.0535
 Frequencies --  1392.4594              1395.2545              1417.6189
 Frequencies --  1466.3295              1473.4333              1494.4942
 Frequencies --  1503.4491              2977.0278              3046.9875
 Frequencies --  3050.4299              3072.5666              3074.9039
 Frequencies --  3084.9030              3104.6156              3112.2284
 Frequencies --  3124.8900              3186.1325              3849.6133


TS5
 Frequencies -- -1644.6112                98.1503               145.5022
 Frequencies --   198.3531               291.4494               301.1606
 Frequencies --   383.2755               406.1628               450.6552
 Frequencies --   474.7208               587.4131               678.4493
 Frequencies --   736.8184               778.3394               840.5335
 Frequencies --   865.5082               878.5253               924.9305
 Frequencies --   954.3240               989.7485              1050.2041
 Frequencies --  1058.8924              1066.3850              1107.6176
 Frequencies --  1121.5112              1153.8329              1210.0632
 Frequencies --  1223.9287              1274.2971              1302.6150
 Frequencies --  1339.7467              1374.4344              1381.8174
 Frequencies --  1386.5177              1389.2491              1416.3879
 Frequencies --  1439.7369              1478.2555              1495.8909
 Frequencies --  1504.6156              2947.6305              2994.7265
 Frequencies --  3050.1082              3052.8566              3073.1601
 Frequencies --  3075.4376              3113.0521              3119.5534
 Frequencies --  3125.1889              3209.3164              3887.5605
```

5product
 Frequencies --   120.9339   146.1401   251.4844
 Frequencies --   271.3855   348.1585   376.4851
 Frequencies --   411.0405   462.2299   486.6225
 Frequencies --   595.1277   681.6280   775.4923
 Frequencies --   828.3427   850.4012   878.9459
 Frequencies --   905.8709   952.5543   1020.3379
 Frequencies -- 1026.2679   1050.7002   1112.2113
 Frequencies -- 1116.9735   1152.7739   1181.9429
 Frequencies -- 1211.6326   1248.1626   1263.6229
 Frequencies -- 1293.6492   1301.5498   1331.4436
 Frequencies -- 1335.5712   1356.8135   1375.2616
 Frequencies -- 1387.2601   1394.2696   1436.9304
 Frequencies -- 1479.2344   1485.8742   1501.2427
 Frequencies -- 1510.6951   3006.8319   3037.4427
 Frequencies -- 3052.0896   3078.8258   3080.1308
 Frequencies -- 3094.3914   3111.5439   3123.8979
 Frequencies -- 3128.3283   3146.2668   3856.2970

6reactant
 Frequencies --   100.5033   129.1444   164.7855
 Frequencies --   177.9654   256.7105   280.6461
 Frequencies --   385.9478   406.0604   430.1018
 Frequencies --   488.1940   538.5475   744.6091
 Frequencies --   777.2369   841.2743   867.2523
 Frequencies --   894.1891   896.9302   947.9071
 Frequencies -- 1002.9967   1034.3154   1049.7511
 Frequencies -- 1081.7597   1137.7266   1140.3631
 Frequencies -- 1155.4241   1198.1639   1274.2638
 Frequencies -- 1295.1199   1315.9565   1328.1543
 Frequencies -- 1352.8307   1369.7462   1382.0211
 Frequencies -- 1386.9576   1400.8457   1426.3252
 Frequencies -- 1462.3374   1474.1892   1485.0407
 Frequencies -- 1498.5305   2992.5884   2998.0784
 Frequencies -- 3043.4011   3069.8533   3080.8957
 Frequencies -- 3096.2419   3113.3489   3123.3991
 Frequencies -- 3131.9312   3229.0706   3855.4204

TS6
 Frequencies -- -2111.1823   148.3433   235.1455
 Frequencies --   252.0870   304.6727   339.5359
 Frequencies --   382.0866   400.2804   426.7500
 Frequencies --   524.7395   551.6211   663.3613
 Frequencies --   734.4559   804.9066   855.2690
 Frequencies --   859.7320   883.7300   904.7584
 Frequencies --   975.3778   1004.7350   1032.5982
 Frequencies -- 1041.9054   1084.9084   1105.9892
 Frequencies -- 1109.0771   1139.3238   1197.6189
 Frequencies -- 1240.9189   1277.2839   1326.2148
 Frequencies -- 1339.2850   1347.2271   1360.7557
 Frequencies -- 1383.0202   1390.0526   1403.6324
 Frequencies -- 1461.7533   1468.5938   1482.7410
 Frequencies -- 1504.5818   2973.3412   3017.1307
 Frequencies -- 3037.3260   3050.4494   3075.9223
 Frequencies -- 3103.0174   3107.2982   3117.5674

```
 Frequencies --  3126.5813              3202.5916              3767.4919


6product
 Frequencies --   145.9965               193.9363               280.0503
 Frequencies --   323.6979               359.5668               394.5738
 Frequencies --   423.7222               433.2925               511.6757
 Frequencies --   577.7863               699.4126               770.3358
 Frequencies --   835.3385               853.9004               863.1033
 Frequencies --   886.4663               947.6827               976.2977
 Frequencies --  1013.8341              1036.9596              1083.3918
 Frequencies --  1090.3876              1106.0383              1146.8025
 Frequencies --  1187.6971              1241.2975              1269.3491
 Frequencies --  1277.6242              1301.6213              1327.1106
 Frequencies --  1348.5544              1363.9869              1378.7230
 Frequencies --  1394.0475              1412.4649              1437.0614
 Frequencies --  1465.6646              1477.1962              1492.3172
 Frequencies --  1503.0022              3007.4831              3047.9961
 Frequencies --  3054.5124              3070.9324              3073.6790
 Frequencies --  3084.9278              3110.5819              3114.4571
 Frequencies --  3118.7707              3139.9738              3831.0121
```

Appendix F: M06-2X/6-311++G(d,p) frequencies of propyl systems (cm^{-1}).

```
9reactant/9-22reactant
 Frequencies --    54.9228               117.2363               158.7089
 Frequencies --   180.3643               244.5609               395.0853
 Frequencies --   418.1970               613.4150               897.3526
 Frequencies --   907.9319               955.9129               996.7870
 Frequencies --  1047.0856              1146.7354              1159.9698
 Frequencies --  1291.4273              1373.6078              1385.2289
 Frequencies --  1406.5548              1420.1829              1470.3341
 Frequencies --  1479.1574              1490.3505              3021.2838
 Frequencies --  3035.9773              3080.8231              3096.1285
 Frequencies --  3138.7340              3220.9646              3860.1502

TS9
 Frequencies -- -1637.9893               129.3294               158.1825
 Frequencies --   204.8463               293.6728               391.4578
 Frequencies --   410.3579               552.1176               734.5471
 Frequencies --   834.5185               927.1390               950.9434
 Frequencies --  1017.7321              1078.6461              1161.4663
 Frequencies --  1165.5382              1211.4050              1311.5617
 Frequencies --  1371.2929              1424.9381              1461.3727
 Frequencies --  1477.2631              1499.2022              2978.8111
 Frequencies --  3004.8084              3051.9878              3102.1514
 Frequencies --  3154.6793              3211.5965              3887.4457


9product
 Frequencies --   145.2608               224.9649               255.4696
 Frequencies --   361.3161               444.9897               471.0767
 Frequencies --   535.6387               807.8801               861.7841
 Frequencies --   949.7601              1053.4704              1083.3053
 Frequencies --  1099.7174              1178.9787              1206.1786
```

```
 Frequencies --  1290.3872              1301.0730              1365.7701
 Frequencies --  1389.4780              1402.3701              1447.0183
 Frequencies --  1488.4249              1505.6199              2931.8770
 Frequencies --  3016.5852              3031.8824              3067.6630
 Frequencies --  3142.9636              3157.7500              3860.4447


TS9-22
 Frequencies --  -905.8659                62.1018               151.5825
 Frequencies --   190.1748               195.4832               269.4643
 Frequencies --   306.3600               424.7664               655.3347
 Frequencies --   664.8892               796.4329               903.8932
 Frequencies --   942.9357               982.6491              1063.3684
 Frequencies --  1128.6269              1249.1710              1293.8776
 Frequencies --  1367.5059              1397.9832              1429.8628
 Frequencies --  1461.4397              1469.7346              2678.3516
 Frequencies --  3002.1692              3014.9732              3080.6137
 Frequencies --  3168.2981              3198.1221              3874.8332



9-22product1
 Frequencies --   142.4716               235.4660               264.6445
 Frequencies --   671.5778               676.8170               871.4291
 Frequencies --   905.2937              1008.1648              1120.0020
 Frequencies --  1152.7801              1282.0674              1372.0026
 Frequencies --  1413.0607              1427.9953              1457.4228
 Frequencies --  1498.6071              1504.7635              1866.2973
 Frequencies --  2944.5214              3049.3176              3078.4716
 Frequencies --  3080.3699              3155.6148              3157.1796


OH
Frequencies --  3791.3262


8reactant
 Frequencies --   -17.0689               104.9061               131.0604
 Frequencies --   168.7153               280.3456               385.2386
 Frequencies --   463.8027               555.5004               755.5831
 Frequencies --   889.2136               943.8851              1038.7686
 Frequencies --  1093.4770              1107.8433              1155.4026
 Frequencies --  1248.7185              1317.7966              1329.3857
 Frequencies --  1396.9289              1425.5793              1467.2922
 Frequencies --  1479.6631              1487.4042              3017.8064
 Frequencies --  3049.2994              3101.9037              3125.6728
 Frequencies --  3171.6253              3279.7018              3857.8339


TS8
 Frequencies -- -2302.0403               177.6279               309.9302
 Frequencies --   376.8441               417.2915               456.7378
 Frequencies --   517.2297               549.9250               800.9400
 Frequencies --   881.0847               890.4918               929.0770
 Frequencies --  1018.3940              1046.6534              1084.8021
 Frequencies --  1173.1477              1220.1502              1275.2487
 Frequencies --  1341.9102              1389.6706              1460.1862
```

```
 Frequencies --  1476.1752              1493.8029              3024.6123
 Frequencies --  3031.2548              3080.1077              3103.4477
 Frequencies --  3162.1461              3268.5177              3817.3895


8product
 Frequencies --    90.8349               194.3094               261.6371
 Frequencies --   278.4277               423.2728               539.9612
 Frequencies --   679.2851               857.4001               902.9635
 Frequencies --   994.1940              1070.4007              1079.1517
 Frequencies --  1103.5387              1153.7946              1230.7941
 Frequencies --  1260.1809              1318.5766              1338.6287
 Frequencies --  1386.7025              1390.5177              1456.2137
 Frequencies --  1471.6596              1527.6024              2943.3456
 Frequencies --  3015.1778              3040.4375              3070.4506
 Frequencies --  3085.6586              3122.6229              3921.6317


4reactant/4-2reactant
 Frequencies --    96.0736               156.6839               224.6578
 Frequencies --   230.9351               291.9919               343.3192
 Frequencies --   452.2597               491.3033               569.5799
 Frequencies --   859.4024               925.1691               938.7899
 Frequencies --  1036.2950              1081.9259              1176.3800
 Frequencies --  1190.2371              1339.8936              1382.6862
 Frequencies --  1400.7675              1406.9540              1462.0035
 Frequencies --  1488.3815              1500.5468              3071.6710
 Frequencies --  3083.2047              3152.6339              3158.5068
 Frequencies --  3167.7952              3285.2069              3831.6297


TS4
 Frequencies -- -2757.1288               161.2912               230.6796
 Frequencies --   358.7476               368.7994               403.0927
 Frequencies --   457.4167               512.9285               620.1167
 Frequencies --   842.2562               874.6074               932.4731
 Frequencies --   954.2761              1013.6832              1063.8265
 Frequencies --  1105.9031              1193.8926              1241.4659
 Frequencies --  1347.0276              1408.7092              1470.2198
 Frequencies --  1493.0707              1502.1829              2989.8975
 Frequencies --  3067.9606              3145.7949              3161.6019
 Frequencies --  3165.3583              3284.6558              3878.9763


4product
 Frequencies --   136.4161               199.6087               252.9285
 Frequencies --   365.1578               433.5410               457.5183
 Frequencies --   523.7577               845.2331               892.9553
 Frequencies --   941.4572              1043.1778              1118.4303
 Frequencies --  1130.7295              1147.1070              1178.5803
 Frequencies --  1212.9916              1290.9612              1361.9938
 Frequencies --  1398.8079              1426.5496              1489.5094
 Frequencies --  1499.2799              1513.8741              2922.2915
 Frequencies --  3025.3125              3070.6209              3126.8259
 Frequencies --  3146.1515              3162.3586              3860.3596
```

TS4-2

Frequencies --	-1537.7731	102.4331	171.0155
Frequencies --	185.7567	209.9395	324.3020
Frequencies --	394.8929	478.8801	486.9993
Frequencies --	623.6646	767.0262	846.7825
Frequencies --	903.7445	955.3184	1025.1933
Frequencies --	1060.9384	1128.3521	1291.9503
Frequencies --	1391.8699	1401.4809	1458.6431
Frequencies --	1485.9943	1506.7098	2458.8835
Frequencies --	3076.6420	3157.6481	3169.7553
Frequencies --	3176.9498	3303.1034	3870.6446

4-2product1

Frequencies --	45.6309	132.4199	382.0581
Frequencies --	488.4321	541.5059	804.9754
Frequencies --	882.0415	898.2109	1085.5339
Frequencies --	1121.4370	1249.5419	1388.3001
Frequencies --	1398.2947	1465.3664	1468.1872
Frequencies --	1475.7869	1491.7736	1857.4396
Frequencies --	3063.9396	3069.1408	3129.9880
Frequencies --	3136.1421	3182.7538	3183.6816