Dynamics of Peroxy and Alkenyl Radicals Undergoing Competing Rearrangements in Biodiesel Combustion

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I. Overview

The ignition of diesel fuel depends on isomerization of peroxy radicals (ROO•) via a hydrogen shift reaction:

$$ROO^{\bullet} \rightarrow QOOH \quad (1)$$

Production of OH radical by chain propagation following reaction (1) contributes to autoignition:

$$QOOH \rightarrow \text{cyclic ether} + OH \quad (2)$$

but chain branching (the sequence of reactions 3-6) is critical to autoignition because it produces two OH radicals:

$$QOOH + O_2 \rightarrow {}^{\bullet}OOQOOH \quad (3)$$

$$^{\bullet}OOQOOH \rightarrow HOOPOOH \quad (4)$$

$$HOOPOOH \rightarrow HOOP{=}O + OH \quad (5)$$

$$HOOP{=}O \rightarrow HO^{\bullet} + {}^{\bullet}OP{=}O \quad (6)$$

Processes such as reaction (7):

$$ROO^{\bullet} \rightarrow \text{alkene} + HOO^{\bullet} \quad (7)$$

compete with chain branching. Experimentalists face several difficulties in gaining an understanding of this chemistry, and only one QOOH species has ever been detected by experiment! This has inspired many computational studies of these processes.

Biodiesel fuel is increasingly being used worldwide. Although we have a fair understanding of the molecular details of the chemistry of peroxy radicals derived from alkanes, biodiesel fuels contain ester and olefin groups which significantly impact the thermodynamics and kinetics of biodiesel ignition. The broader goal of this research is to carry out systematic computational studies of the elementary kinetics of the chemistry of R•, ROO•, QOOH and •OOQOOH compounds that are models for biodiesel ignition.

Carbon-centered radicals such as R• and QOOH can undergo well-known 1,n H-shift reactions, e.g.:

$$^{\bullet}CH_2(CH_2)_3CH(CH_3)_2 \rightarrow CH_3(CH_2)_3C^{\bullet}(CH_3)_2 \quad (8)$$

which are known to be able to change the structure of the radical from that initially formed. A competing set of reactions, shown in Scheme 1, can isomerize carbon-centered radicals formed in the vicinity of a double bond. Results from the literature indicate these reactions may compete with 1,n H-shift reactions. We will use computational chemistry to explore the importance of these reactions and analogous cyclization reactions of peroxy radicals in model compounds of biodiesel fuel.

II. Recent Progress

A) Cis-trans Isomerization of Allylic Radicals

Biodiesel fuel is composed largely of fatty acid methyl esters. The fatty acids are composed of long hydrocarbon chains, which are usually unsaturated. These double bonds are almost exclusively in cis configurations. By contrast, gaseous alkenes studied in combustion are mostly trans. Bounaceur, et al,[1] argued that the thermal cis-trans isomerization was unimportant, but did not actually calculate rate

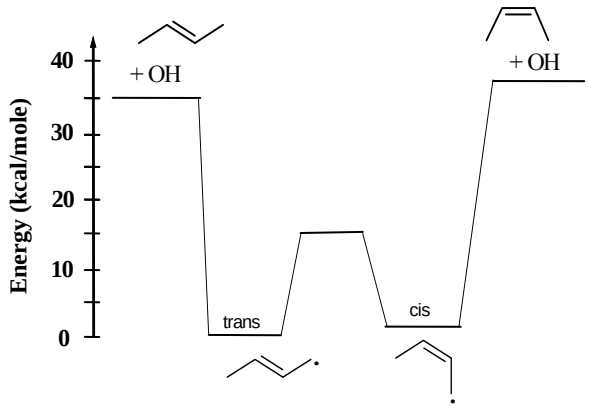


Figure 1. Potential energy profile for 2-butene + OH at M05-2X/6-311+G(2df,2p).

constants. At temperatures of 700 K and higher, the thermal rate constant for isomerization should out-compete addition of O_2 to these radicals.

At lower temperatures, chemically activated isomerization can be extensive. The potential energy profile for production of the 2-butenyl radical ($CH_3CHCHCH_2$) from OH + 2- butene is shown below in Figure 1. RRKM-Master Equation calculations were carried out with the MultiWell program[2] to determine the fate of chemically activated 2-butenyl radical formed from OH + *trans*-2-butene. In simulations at a range of pressures and temperatures, the *cis* isomer was quite abundant, if not dominant, over the trans isomer.

This result is counterintuitive, because it shows that the isomer which is thermodynamically less stable (at low temperature) is preferred. However, in this case, the key factor is the ratio, $R_{DOS}(E)$, of the density of states, $\rho(E)$, of the two isomers at a range of energies above the isomerization barrier at which the isomerization rate constant becomes smaller than quenching. This density of states generally favors the *cis* isomer.

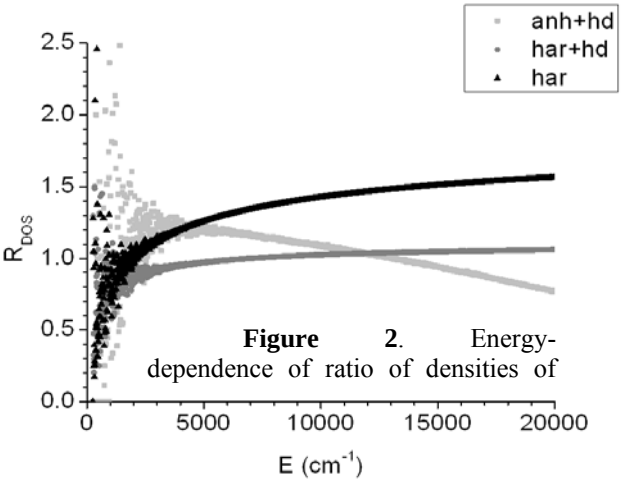


Figure 2. Ratio of density of states of cis to trans isomer of 1-methylallyl radical versus energy of the trans isomer.

The shape of $R_{DOS}(E)$ varies with the quantum chemical method used and the extent to which the harmonic oscillator approximation is invoked. The results at M06-2X/6-311+G(2df,2p) are shown at left, starting with highly energized radicals formed in N_2 bath gas at 300 K. Different symbols indicate different methods of calculating densities of states: har = all modes treated as harmonic oscillators; har+hd = as har but methyl torsion treated as hindered rotor; anh+hd = anharmonic treatment except methyl torsion.

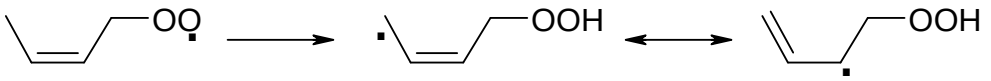
The method dependence of R_{DOS} at energies just above the barrier to isomerization (~15 kcal/mol or ~5,500 cm^{-1}) is reflected in the cis:trans ratio of quenched radicals. For the quantum chemical method used in Figure 2, the cis:trans ratio decreases in the order har ≳ anh+hd > har+hd. These results were published in Ref. 3.

B) Unimolecular Reactions of the Allylic Four-Carbon Peroxy Radical

We have carried out M05-2X and CBS-QB3 calculations on the reactions of the *cis*- and *trans*-but-2-en-1-peroxy radical formed by O_2 addition to C_1 of 2-butenyl radical:

$$[CH_3CH{=}CHCH_2\bullet \leftrightarrow CH_3CH\bullet CH{=}CH_2] + O_2 \rightarrow CH_3CH{=}CHCH_2OO\bullet \quad (9)$$

This is a larger analog of allyl radical. Allyl radical adds O_2 but the resulting peroxy radical back-dissociates rather than reacting further. Only the cis isomer of the product of this reaction has the potential to undergo an H-shift reaction:



(10)

that could propagate radical chemistry and lead to autoignition of diesel fuel. The results above indicate that one should expect the cis isomer to be formed, even starting from trans alkenes. The quantum chemical results indicate that loss of O_2 (reaction -9) is ~3 kcal/mol favored over reaction (10). Given that reaction (-9) has a higher Arrhenius pre-exponential term than reaction (10), loss of O_2 will be favored under all conditions.

C) Autoignition Mechanism of Methyl Butanoate (MB)

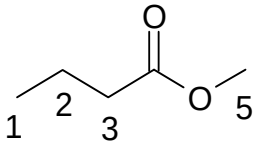


Figure 3. Methyl butanoate

Methyl butanoate (MB) is composed of a methyl ester group and a short alkyl group (see Figure 3). MB oxidation mechanism has been studied as the starting point for understanding biodiesel combustion for a decade.[4] The CBS-QB3 composite method is used to determine reaction energies and activation barriers to reactions of peroxy radicals and the corresponding QOOH species. We include all four peroxy radicals formed subsequent to H-atom abstraction from MB (sites 1-3 and 5 in Figure 3). Reactions treated include H-shift and HO_2 elimination of ROO•, and decomposition of QOOH by C-C, C-O, and O-O scission.

Potential energy profiles have been obtained for all four peroxy radicals. Where one of these peroxy radicals isomerizes to form a carbon-centered radical, the chemistry of the second-generation peroxy radical has been investigated. Results are shown in Figure 4 for a single case.

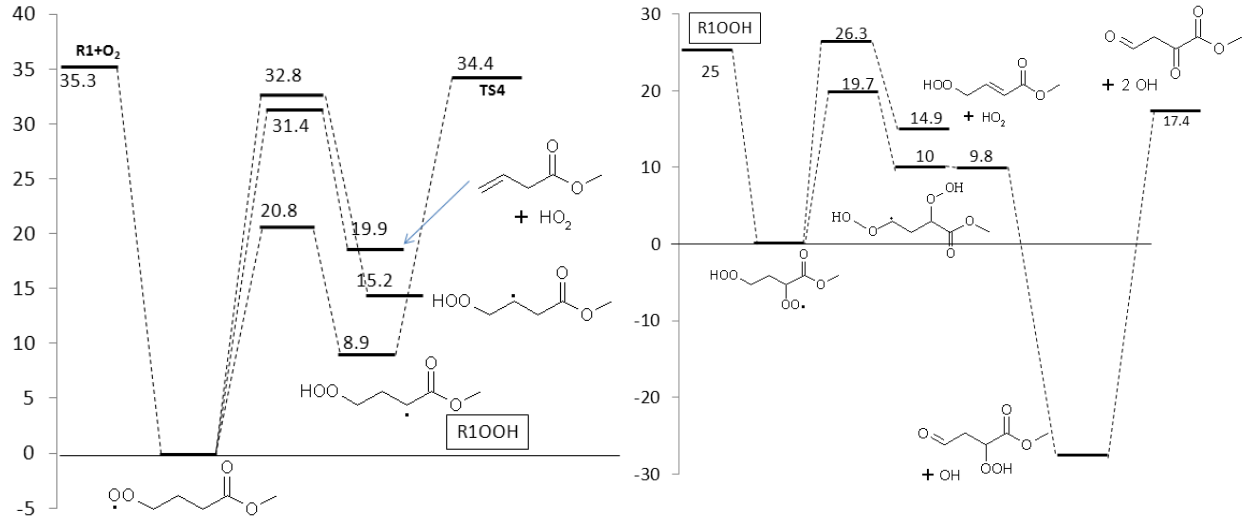


Figure 4. Potential energy profiles (kcal/mol, corrected for zero-point energy) for chemistry following H-abstraction from site 1 of MB. LEFT: competing reactions of the peroxy radical. RIGHT: competing reactions R1OOH, which is the kinetically favored product of the reactions shown at left.

Clearly, for this case, the most favorable reaction for the initially-formed peroxy radical is to isomerize to the structure labeled R1OOH, which cannot undergo further unimolecular reactions. Addition of O_2 to R1OOH leads to a second generation peroxy radical. This species has the potential to isomerize, followed by prompt loss of OH and generation of a highly oxidized stable

organic molecule. A hydrogen-bonded complex between OH and the terminal carbonyl group complicates the potential energy profile. High-pressure limiting rate constants have been calculated for unimolecular reactions relevant to the fate of all four primary peroxy radicals and any second generation peroxy radicals. Investigations of reactions of chemically activated radicals are ongoing.

We went on to study the fate of the •OOQOOH radicals produced following the favored 1,n H-shift reactions of methylbutanoate (MB). We find peroxy radical interconversions of •OOQOOH radicals (•OOQOOH → HOOQOO•) commonly possess the lowest barriers of any unimolecular reaction of these radicals, despite that they proceed via 8-, 10- and 11-member ring transition states. At temperatures relevant to autoignition, these peroxy radical interconversions are dominant or significant reaction pathways. This means that •OOQOOH radicals that were expected to be produced in negligible yields are, instead, major products in the autoignition of methyl butanoate. These reactions have not previously been considered for OOQOOH from MB, and will require revision of models of autoignition of methylbutanoate and other esters.

A harmonic oscillator (HO) treatment of the multiple torsional modes of these large molecules may lead to large errors in computed rate constants. Treating the torsions as separable hindered rotors (HR) provides an approximate correction. From Figure 5, it can be seen that the HR treatment of the torsions leads to much different rate constants than the HO treatment.

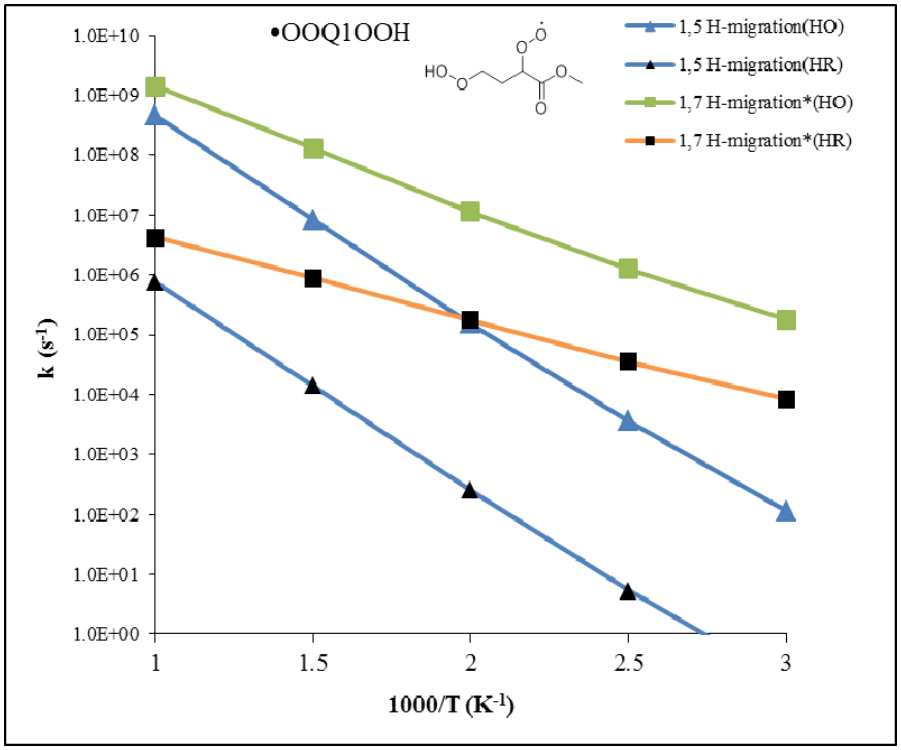


Figure 5. Rate constants for the two fastest reactions of •OOQ1OOH including the 1-D hindered rotor treatment (HR) or using the harmonic oscillator approximation (HO) on both reactants and transition states. The asterisk indicates peroxy radical interconversion: •OOQOOH → HOOQOO•.

D) Tunneling in the 1,5 H-shift of the a Model for First and Second-Generation Peroxy Radicals

Consider the 1,5 H-shift reaction in propylperoxy radical (reaction 11) and in the peroxy radical formed subsequent to its isomerization (reaction 13):

$$CH_3CH_2CH_2OO\bullet \rightarrow \bullet CH_2CH_2CH_2OOH \qquad (11)$$

$$O_2 + \bullet CH_2CH_2CH_2OOH \rightarrow \bullet OOCH_2CH_2CH_2OOH \quad (12)$$

$$\bullet OOCH_2CH_2CH_2OOH \rightarrow [HOOCH_2CH_2CH\bullet OOH] \rightarrow HOOCH_2CH_2CH{=}O + \bullet OH \quad (13)$$

The species $HOOCH_2CH_2CH\bullet OOH$ may or may not be a minimum on the potential energy surface, but even if it is, it likely lives for picoseconds or less.[5] Reaction (13) and analogous reactions are very exothermic on account of the loss of OH radical and formation of a carbonyl compound. Tunneling calculations in such cases commonly invoke the asymmetric Eckart formula and use this large exothermicity as a parameter which influences the extent of tunneling. Quantum chemical calculations have been carried out for this system. These results were published in Refs. 6 and 7. The asymmetric Eckart tunneling approximation worked very well in the limit of high-pressure, as judged by its agreement with results of tunneling calculations using small-curvature tunneling.

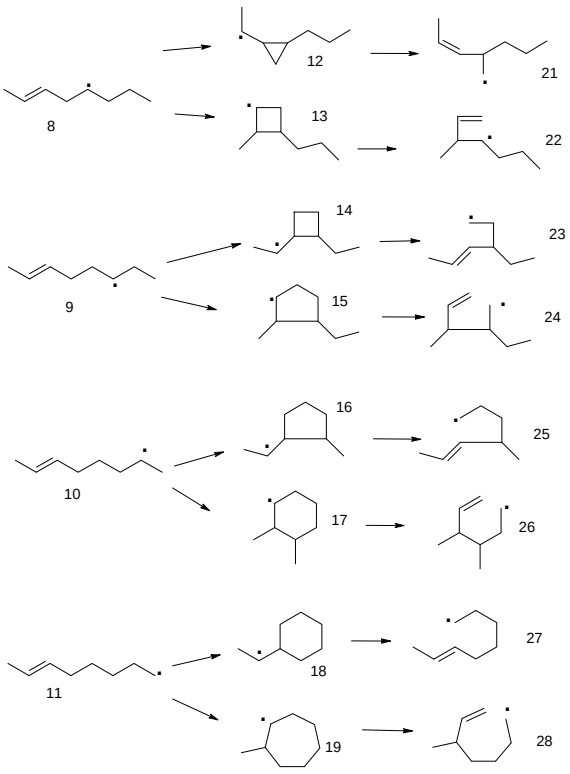
E) Cyclization-Decyclization Reactions of Unsaturated Hydrocarbon Radicals

Cyclization reactions of unsaturated radicals are well known in the organic chemistry literature. The cyclization reactions are labeled *endo* if the radical center of the product is on a carbon *in* the ring, and *exo* if the radical center is not in the ring. We surveyed a broad range of reactions at the CBS-QB3 level of theory, only a few of which are shown below in Scheme 2. The products of cyclization of the *n*-octenyl radicals will potentially decyclize to form branched octenyl radicals (see Scheme 2). In general, branched and straight chain fuels exhibit different ignition behavior. If the chemistry suggested here is important in combustion, and then it needs to be included in kinetic models if those models are to accurately represent combustion behavior.

As can be seen from Table 1, many of the cyclization reactions shown in Scheme 2 possess low barriers, so that these reactions are expected to proceed with high rate constants. Curiously, the decyclization reactions of exo-ring systems (e.g, 12→21) have significantly lower barriers than the decyclization reactions of the endo-ring system of the same ring size (e.g, 13→22). This result appears consisted across 4-, 5-, and 6-member rings.

Rate constants for these reactions were computed using standard transition state theory using the harmonic oscillator rigid-rotor approximation. These rate constants confirm the importance of many of these reactions in comparison to competing unimolecular reactions. The present work represents a much wider survey of these reactions than has been reported previously.

We have also begun looking at radicals produced by hydrogen abstraction from di-olefins, such as linoleic acid. The model



Scheme 2. Examples of exo and endo cyclization reactions of n-octenyl radicals, plus de-cyclization reactions leading to new products.

compound is 2,5-nonadiene with a hydrogen abstracted from one of the carbon atoms. Reactions lead to cyclic radicals, formation of branched species, and formation of allylic radicals starting from non-allylic radicals

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Table 1. Barrier heights (CBS-QB3 values in kcal/mol at 0 K including zero-point energy) for endo- and exo-cyclization and decylization reactions of n-octenyl radicals and the products of their cyclization reactions. Numbers correspond to the identity of species in Scheme 2. The notations "c" and "t" after a number corresponds to the cis and trans isomer, respectively.

Transition State	Reaction type	Forward Barrier	Reverse Barrier
TS_8-12c	exo-trig cyclization	9.1	6.1
TS_8-12t	exo-trig cyclization	9.6	7.0
TS_8-13c	endo-tet cyclization	30.2	24.7
TS_8-13t	endo-tet cyclization	29.0	24.9
TS_9-14c	exo-tet cyclization	14.4	11.0
TS_9-14t	exo-tet cyclization	14.1	12.2
TS_9-15c	endo-pent cyclization	13.6	29.6
TS_9-15t	endo-pent cyclization	14.0	31.6
TS_10-16c	exo-pent cyclization	6.1	20.9
TS_10-16t	exo-pent cyclization	5.9	21.8
TS_10-17c	endo-hex cyclization	6.9	26.1
TS_10-17t	endo-hex cyclization	6.7	27.3
TS_11-18	exo-hex cyclization	7.5	29.3
TS_11-19	endo-hept cyclization	10.8	24.6
TS_12c-21	decyc of 3 member ring	6.2	8.5
TS_12t-21	decyc of 3 member ring	6.3	8.6
TS_13c-22	decyc of 4 member ring	26.3	30.4
TS_13t-22	decyc of 4 member ring	26.9	30.0
TS_14c-23	decyc of 4 member ring	13.1	13.6
TS_14t-23	decyc of 4 member ring	12.7	14.7
TS_15c-24	decyc of 5 member ring	34.1	14.8
TS_15t-24	decyc of 5 member ring	34.2	12.9
TS_16c-25	decyc of 5 member ring	22.1	5.5
TS_16t-25	decyc of 5 member ring	21.7	5.3
TS_17c-26	decyc of 6 member ring	29.6	7.2
TS_17t-26	decyc of 6 member ring	30.0	7.2
TS_18-27	decyc of 6 member ring	50.7	30.1
TS_19-28	decyc of 7 member ring	27.6	13.1

III. Conclusions

This work has shown that cis and trans isomers of allylic radicals can rapidly isomerize. This complicates chemical mechanisms for modeling combustion of alkenes and most of the biofuels derived from triglycerides. We have further found that the peroxy radicals produced when allylic radicals react with O_2 cannot readily undergo further unimolecular reactions. Instead, they will likely back-react to re-generate the allylic radical.

For methylbutanoate, we have found some unexpected chemistry as well as verifying much expected chemistry. Of particular interest is the isomerization of second-generation peroxy radicals (•OOQOOH) to peroxy radicals that were not expected to form.

Rigorous calculations of tunneling in prototypical first-and second-generation peroxy radicals were carried out alongside th Eckart tunneling model, a computationally inexpensive approach widely used in predictive chemical kinetics. The Eckart model was shown to perform well in comparison to more rigorous methods. This should bolster confidence in past and future use of the Eckart approach in modeling combustion kinetics.

Finally, we carried out calculations on the exo and endo ring cyclization/decyclization reactions of octenyl radicals, which are models for radicals produced in combustion of fatty acid methyl esters (biodiesel). The results of these calculations will further our understanding of biodiesel combustion chemistry.

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