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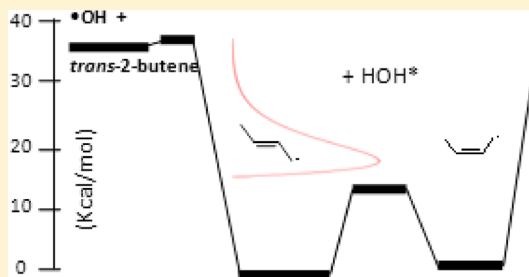
Cis–Trans Isomerization of Chemically Activated 1-Methylallyl Radical and Fate of the Resulting 2-Buten-1-peroxy Radical

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Supporting Information

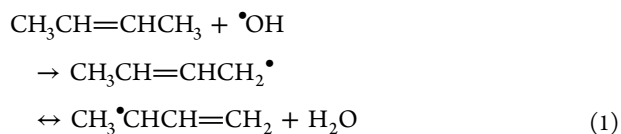
ABSTRACT: The cis–trans isomerization of chemically activated 1-methylallyl is investigated using RRKM/Master Equation methods for a range of pressures and temperatures. This system is a prototype for a large range of allylic radicals formed from highly exothermic (~ 35 kcal/mol) OH + alkene reactions. Energies, vibrational frequencies, anharmonic constants, and the torsional potential of the methyl group are computed with density functional theory for both isomers and the transition state connecting them. Chemically activated radicals are found to undergo rapid cis–trans isomerization leading to stabilization of significant amounts of both isomers. In addition, the thermal rate constant for trans \rightarrow cis isomerization of 1-methylallyl is computed to be high enough to dominate reaction with O_2 in 10 atm of air at 700 K, so models of the chemistry of the (more abundant and more commonly studied) *trans*-alkenes may need to be modified to include the cis isomers of the corresponding allylic radicals. Addition of molecular oxygen to 1-methylallyl radical can form 2-butene-1-peroxy radical ($CH_3CH=CHCH_2OO^\bullet$), and quantum chemistry is used to thoroughly explore the possible unimolecular reactions of the cis and trans isomers of this radical. The cis isomer of the 2-butene-1-peroxy radical has the lowest barrier (via 1,6 H-shift) to further reaction, but this barrier appears to be too high to compete with loss of O_2 .



1. INTRODUCTION

Alkenes studied in flames and reactors are typically dominated by the thermodynamically more stable *trans* isomers, whereas the fatty acid methyl esters (FAMES) that constitute a major form of biodiesel fuel are dominated by *cis* isomers.¹ A major pathway for reaction of alkenes at combustion temperatures (minor under atmospheric conditions) is hydrogen atom abstraction from allylic sites, leading to the formation of allylic radicals.^{2,3} The allylic radical initially formed will possess the same configuration as the parent alkene. Therefore, one might doubt that an understanding of the combustion chemistry of simple alkenes would transfer completely and accurately to the olefin groups of FAMES.

An implicit assumption of the previous statement is that allylic radicals formed by radical attack on alkenes retain the configuration of the parent for the time it takes to undergo further reaction. This assumption was explicitly considered by Bounaceur et al.,² who argued from quantum calculations that the barrier to trans \rightarrow cis isomerization of the pent-2-en-1-yl radical was too large (~ 15 kcal/mol) for that reaction to compete with O_2 addition to form peroxy radicals. Unfortunately, their kinetic analysis neglected the fact that allylic radicals formed in hydrogen abstraction by OH radical, e.g.,

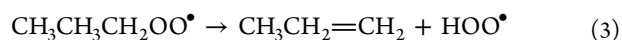


might be expected to possess much of the ~ 36 kcal/mol exothermicity of this reaction.^{4,5} These chemically activated radicals might undergo prompt cis–trans isomerization on a subnanosecond time scale in competition with collisional quenching. The first part of this paper deals with the cis:trans population ratio of the quenched 1-methylallyl radical formed in reaction 1.

The ignition of diesel fuel depends on isomerization of peroxy radicals via intramolecular hydrogen-atom abstraction (1,*n* H-shift), e.g.,



The products of these reactions are generically referred to as QOOH. Production of more than one OH radical (chain branching) in the chemistry following reaction 1 leads to autoignition.⁶ However, other reactions compete with 1,*n* H-shifts and consequently delay the autoignition, such as



This detailed mechanisms of this chemistry has been studied extensively for radicals derived from alkanes but less so for radicals with functional groups.⁷ Although carbon-centered radicals typically add molecular oxygen to form peroxy radicals, resonance stabilization of allylic radicals means that peroxy

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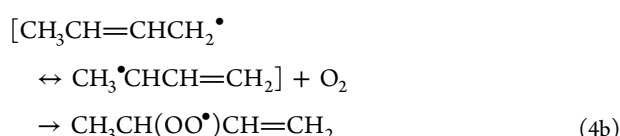
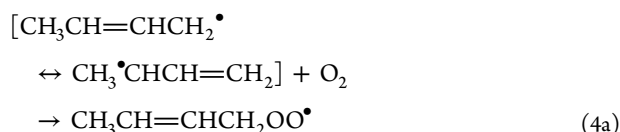
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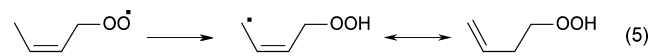
radical formation is less exothermic than for nonallylic radicals. For example, allylperoxy radical ($\text{CH}_2=\text{CHCH}_2\text{OO}^\bullet$) is believed to lose O_2 rather than undergo unimolecular reactions common in other peroxy radicals, such as HOO elimination or 1, n H-shift reactions.⁸ Large allylic peroxy radicals are expected to be produced from the combustion of the fatty acid methyl esters (FAMES),³ which are common constituents of biodiesel fuel.⁹ Peroxy radicals derived from C_5 allylic radicals have been included in kinetic models of combustion^{2,3} and are of importance in isoprene chemistry.^{10–12}

The rate constants and equilibrium constants for the reaction 1-methylallyl + O_2 was studied experimentally by Knyazev and Slagle:¹³



although they could not distinguish between channels 4a and 4b. There do not seem to have been any previous quantum chemical studies of 1-methylallyl + O_2 , but the addition of O_2 to other allylic radicals has been studied.^{8,14–16} In the second part of the paper we thoroughly examine the possible reactions of the *cis* and *trans* isomers of the 2-buten-1-peroxy radical formed in the reaction of the 1-methylallyl radical with O_2 .

The *cis* isomer of the 2-buten-1-peroxy radical ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet$) formed in reaction 4a is of particular interest, because it has the potential for chemistry that is not possible for its *trans* isomer, namely, the 1,6 H-shift reaction:



This reaction potentially leads to autoignition chemistry, where other reactions are expected to have activation barriers too high to compete with loss of O_2 , that is, reaction $-4a$.^{15,16} Reaction $-4b$ is expected to dominate the fate of the 3-buten-2-peroxy radical formed in reaction 4b.

The first part of this work uses RRKM/Master Equation simulations to assess the importance of *trans* \rightarrow *cis* isomerization of the chemically activated *trans*-1-methylallyl radical. Initial results, based on sums and densities of states computed using the harmonic oscillator approximation, suggested that the *cis* isomer would be formed in abundance and would potentially be the dominant isomer of 1-methylallyl radical formed. To validate these results, the method of calculation of sums and densities of states was extended to treat the methyl torsion as a hindered rotor and the vibrations as anharmonic. The extent of formation of quenched *cis*-methylallyl radical from chemically activated *trans*-1-methylallyl radical was considered as a function of temperature, pressure, and the initial internal energy of the radical. Thermal rate constants for *trans* \rightarrow *cis* isomerization were also computed.

2. COMPUTATIONAL DETAILS

All quantum chemical calculations were carried out using the Gaussian09 program.¹⁷ Calculations for free radicals were carried out with the spin-unrestricted formalism. Three density

functionals were used to compute structures and vibrational frequencies for *cis*- and *trans*-1-methylallyl radical and the transition state for *cis*–*trans* isomerization: M05-2X,¹⁸ M06-2X,¹⁹ and the venerable B3LYP functional.^{20,21} The 6-311+G(2df,2p) basis set was used throughout. The effective mass of the methyl torsion was determined using the method of Ayala and Schlegel.²² Anharmonicities, x_{ij} , were calculated using numerical differentiation guided by second-order vibrational perturbation theory (VPT2).^{23–26} The sensitivity of vibrational frequencies to grid size in DFT calculations has been noted²⁷ and may be particularly important for obtaining valid anharmonic force constants. Therefore, all the DFT calculations were performed using a pruned (99 590) grid, which is defined as 99 radial shells and 590 angular points per shell.

$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet$ possesses multiple conformers. A relaxed potential energy scan of the CCCO and CCOO dihedral angles for *cis* and *trans* isomers was performed at the M05-2X/6-31+g(d,p) level of theory to find the lowest energy conformer. Then the lowest energy conformer was reoptimized by the composite CBS-QB3 method.²⁸ The CBS-QB3 method starts by optimizing geometries and determining harmonic vibrational frequencies at B3LYP/6-311G(d,p). This is followed by CCSD(T)/6-31+G(d') single points, extrapolation of the MP2 correlation energy to the basis set limit, and addition of an empirical correction term. CBS-QB3 has been widely used to explore peroxy radical chemistry.^{29–34} In CBS-QB3 calculations, the B3LYP/6-311G(d,p) zero-point energy (ZPE) is scaled by a factor 0.99;²⁹ for the RRKM/Master Equation calculations the vibrational frequencies were not scaled. The nature of saddle points were checked by vibrational analysis and sometimes by IRC calculations.

RRKM/Master Equation calculations on the isomerization of chemically activated 1-methylallyl radical were carried out using the MultiWell program^{35–37} at pressures of 0.01, 0.1, 1, 10, and 100 atm. Temperatures of 300, 500, 700, and 900 K were considered. Sums and densities of states using the harmonic and anharmonic oscillator approximations were computed using the algorithms implemented in the programs *densum*^{38,39} and *adensum*,^{40–42} respectively, which are part of the MultiWell program package. Sums and densities of states were calculated at intervals of 10 cm^{-1} for the lowest 2990 cm^{-1} of each species or transition state and at intervals of 427.1 cm^{-1} for higher energies. All MultiWell simulations started from the *trans* isomer of 1-methylallyl radical, as the *trans* isomer dominates the population of the parent alkene. The methyl torsion, when not treated as a harmonic oscillator, was treated as a symmetrical 1-D hindered rotation of 3-fold symmetry. Multiwell simulations used 10 000 trials to achieve a statistical precision of about 0.005 in the fractional population of *cis* and *trans* isomers.

The pressure dependence of thermal rate constants for *trans* \rightarrow *cis* isomerization of 1-methylallyl was computed by the energy-grained RRKM/Master Equation method within the program package UNIMOL,⁴³ as modified by Miyoshi.⁴⁴ The GPOM program⁴⁵ was used to extract information from Gaussian output files and create formatted UNIMOL input files. These calculations used the harmonic oscillator approximation, except that the methyl torsion was treated as a hindered rotor.

In both sets of RRKM/Master Equation calculations, the bath gas was chosen to mimic N_2 . Lennard-Jones parameters for N_2 are available in the literature.^{46,47} The Lennard-Jones parameters for collisions between 1-methylallyl radical (R) and

N_2 (M) were obtained by following rules, as suggested by Gilbert et al.⁴⁶

$$\sigma_{RM} = \frac{1}{2}(\sigma_R + \sigma_M) \quad (6)$$

$$\varepsilon_{RM} = \sqrt{\varepsilon_R \varepsilon_M} \quad (7)$$

where σ and ε are the Lennard-Jones radius and well-depth, respectively. Values of σ and ε were estimated by following empirical formulas:^{46,47}

$$\sigma_R = 1.45 \left(\sum V_i \right)^{1/3} \quad (8)$$

$$\varepsilon_R(K) = 1.21 T_b \quad (9)$$

Here V_i is the additive volume increment of each atom as tabulated in refs 46 and 47 and T_b is the normal boiling point of each species. Because T_b values for 1-methylallyl radicals are not known, we used the value for *cis*-2-butene.⁴⁸ The resulting σ_R and ε_R values are 5.27 Å and 312 K. Collisional energy transfer was treated with an exponential-down model where the probability of a deactivating collision removing an energy ΔE is proportional to $\exp(-\Delta E/\alpha)$. These calculations assumed $\alpha = 175 \text{ cm}^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Cis–Trans Isomerization of the 1-Methylallyl Radical. Figure 1 depicts the molecular structures of *cis*- and

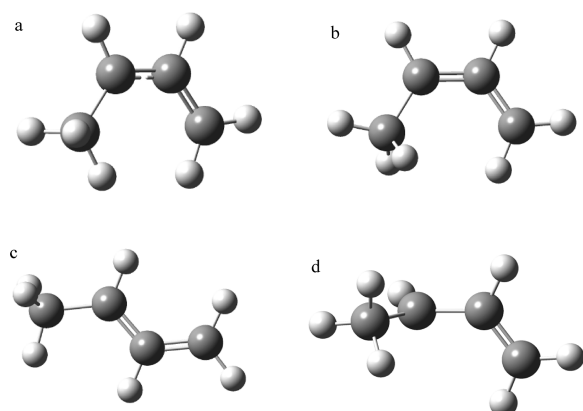


Figure 1. Molecular structures in the 1-methylallyl system: (a) *cis* isomer at M05-2X and M06-2X; (b) *cis* isomer at B3LYP; (c) *trans* isomer; (d) transition state for *cis*–*trans* isomerization.

trans-1-methylallyl radicals and the transition state interconverting them. For the *cis* isomer, M05-2X and M06-2X calculations find the same conformational minimum, with one H atom of the methyl group eclipsing the hydrogen atom on the adjacent carbon atom. In contrast, B3LYP calculations indicate this conformation has an imaginary frequency, and finds a minimum with the methyl group rotated about 60°.

Table 1 provides the relative energies of the *cis*- and *trans*-1-methylallyl radicals and the barrier heights to *cis*–*trans* isomerization computed using three different DFT methods and three different methods of calculating the zero-point energies. Figure 2 depicts the potential energy profile for

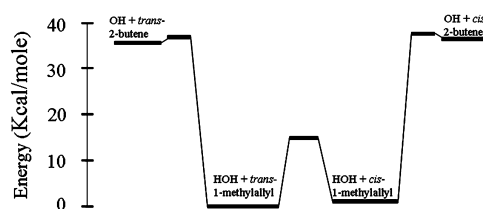


Figure 2. Schematic of the potential energy profile for the *cis*- and *trans*-1-methylallyl radical, their interconversion, and their formation from 2-butene + OH (reaction 1). The exothermicity of reaction 1 is taken from refs 4 and 5 and the activation barrier from ref 58.

reaction 1 and *cis*–*trans* isomerization of 1-methylallyl radical. The *trans* isomer is 0.0–0.9 kcal/mol more stable than the *cis* isomer, and the barrier height for the *trans* → *cis* isomerization is 14.3–16.1 kcal/mol. The computed barrier heights are very consistent with that determined for allyl radical, itself, from experiment ($15.7 \pm 1.0 \text{ kcal/mol}$)⁴⁹ and previous theoretical studies,⁵⁰ as well as values computed for other allylic radicals.⁵¹ Calculations in Multiwell were used to determine the ratio of *cis* to *trans* radicals in thermalized populations of 1-methylallyl radical formed from the chemically activated *trans* isomer. Calculations were initially carried out by assuming the *trans*-1-methylallyl radical possessed a thermal distribution of internal energy shifted upward by 30 kcal/mol, because it was assumed that at least several kcal/mol of the exothermicity of reaction 1 would be partitioned into other degrees of freedom. The dependence of the isomeric ratio on initial energy and the likely distribution of energy in reaction 1 are dealt with later in this section.

Figure 3 shows the *cis*:*trans* ratio of quenched radicals for a temperatures spanning 300–700 K at 1 atm of N_2 bath gas. Simulations were run at 900 K, but the thermal energy at 900 K is above the barrier height, so chemically activated and thermal (steady state) reaction cannot be distinguished. The results

Table 1. Relative Energy of the *Cis* Isomer of the 1-Methylallyl Radical (E_{cis}) and the Saddle Point for Isomerization (E_0) Relative to the *Trans* Isomer at 0 K in kcal/mol with Three Different Functionals Using the 6-311+G(2df,2p) Basis Set; Frequencies of Methyl Torsion ($\nu_{torsion}/\text{cm}^{-1}$) Treated as a Harmonic Oscillator for *Cis* and *Trans* Isomers and the Transition State (TS)^a

method	E_{cis}			E_0			$\nu_{torsion,cis}$	$\nu_{torsion,trans}$	$\nu_{torsion,TS}$
	har	har+hd	anh+hd	har	har+hd	anh+hd			
B3LYP	0.9	0.9	0.9	16.1	16.1	16.0	57	148	100
M05-2X	0.6	0.6	0.0	16.0	16.0	16.0	85	154	94
M06-2X	0.4	0.4	0.7	14.3	14.3	14.5	89	152	110

^aDifferent methods of calculating the sums and densities of states are abbreviated as follows: har = all modes treated as harmonic oscillators; har+hd = harmonic oscillator except for methyl torsion treated as hindered rotor; anh+hd = anharmonic treatment except methyl torsion treated as hindered rotor.

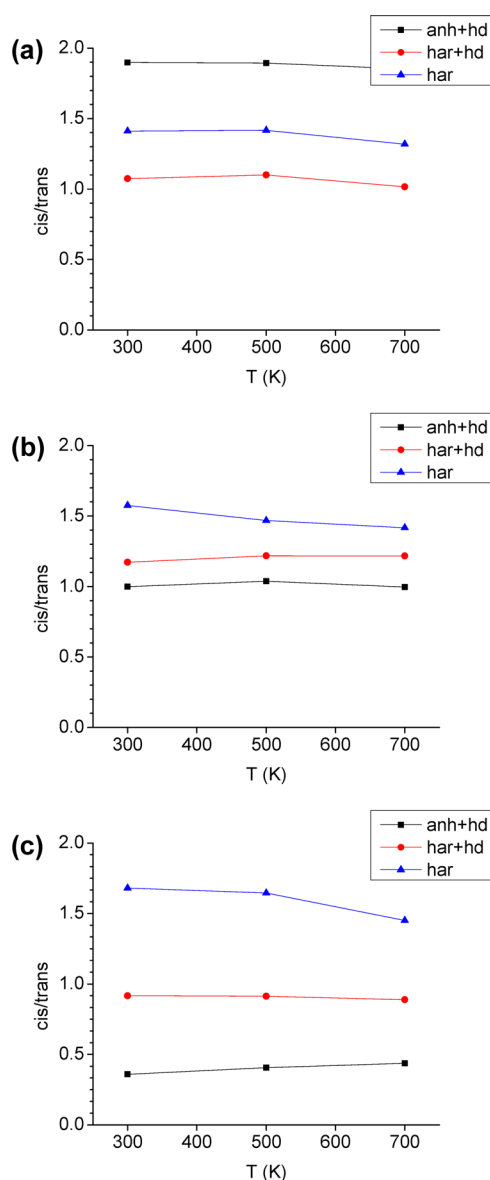


Figure 3. Temperature dependence of the population ratio of quenched 1-methylallyl radicals ($R_{\text{cis:trans}}$) formed in 1 atm of N_2 bath gas from chemically activated trans isomer with a thermal distribution of energy shifted upward by 30 kcal/mol ($\sim 10\,500\text{ cm}^{-1}$) from the zero-point energy: (a) M05-2X, (b) M06-2X, and (c) B3LYP, all with the 6-311+G(2df,2p) basis set. Different symbols indicate different methods of calculating the sums and densities of states: har = all modes treated as harmonic oscillators; har+hd = harmonic oscillator except for methyl torsion treated as hindered rotor; anh+hd = anharmonic treatment except methyl torsion treated as hindered rotor.

depicted in Figure 3 cover two dimensions of methodology: the choice of functional and the method of calculating sums and densities of states. Most significantly, all simulations predict the cis isomer to be quite abundant, if not dominant. Regardless of the treatment of the methyl torsion, the computed cis:trans ratio depends significantly on the functional used. The most disturbing result in Figure 3 is that the anharmonic treatment generates results that differ wildly depending on the functional; by comparison, the effect of adding the hindered rotor treatment to the fully harmonic calculation is smaller and more consistent: the ratio is reduced from a range of 1.4–1.7 to a range of 0.9–1.2.

As reported in Table 1, the fact that the trans isomer is more stable than the cis isomer (at 0 K) might cause one to expect that the trans isomer will dominate the population of quenched radicals, in contrast to the results reported here. In contrast, in the present circumstances, what matters is not the relative energies or free energies at any temperature. Rather, to the extent that isomerization of the chemically activated radicals proceeds faster than quenching to below the barrier, what is more significant is the ratio of microcanonical rate constants:

$$\frac{k(E)_{\text{trans} \rightarrow \text{cis}}}{k(E)_{\text{cis} \rightarrow \text{trans}}} = \frac{\frac{N^*(E-E^*)}{h\rho(E)_{\text{trans}}}}{\frac{N^*(E-E^*)}{h\rho(E-\Delta E)_{\text{cis}}}} = \frac{\rho(E-\Delta E)_{\text{cis}}}{\rho(E)_{\text{trans}}} \quad (10)$$

where N^* is the sum of states at the transition state, E^* is the barrier height, ΔE is the zero-point energy-level difference between the cis and trans isomers, and $\rho(E)_{\text{trans}}$ and $\rho(E-\Delta E)_{\text{cis}}$ are the densities of states of the trans and cis isomers, respectively. This ratio, in turn, depends only on ratios of the densities of states of the two isomers at energies above the ~ 15 kcal/mol barrier to reaction. At such energies, intuition based on low-temperature thermodynamics is not a reliable guide to the relative stability of these isomers. The absence of a strong effect due to the modest differences in barrier heights among the three functionals strengthens this argument.

Consider now the effect of treating the methyl torsion as a hindered rotor: the densities of states are less sensitive to harmonic torsional frequency when treated as a hindered rotor than when treated as a harmonic oscillator. Now consider two points that can be determined from Table 1: first, the harmonic frequency associated with the trans isomer scarcely depends on the functional and always higher than that of the cis isomer; second, the value for the cis isomer calculated at B3LYP is much lower than that calculated at M05-2X or M06-2X (largely because of its different conformational minimum). From the first point we would expect the ratio of the density of states of the cis isomer to the trans isomer to decrease upon including the hindered rotor treatment. Consequently, when using the harmonic oscillator approximation for all modes, one would expect the cis isomer to be favored more when using B3LYP than with other functionals. One would further expect the cis:trans ratio of quenched radicals to be lower when using the hindered rotor treatment. Figure 3 confirms that both expectations are true.

The results above suggest that one explicitly consider how the computed densities of states (DOS) varies with methodology. To enable comparison between DOS and cis:trans ratios, we consider the ratio of the DOS (R_{DOS}) of the cis isomer to that of the trans as a function of energy above the zero-point energy of the trans isomer. Figure 4 plots R_{DOS} versus energy across our two methodological dimensions. Curves of $R_{\text{DOS}}(E)$ computed using the harmonic oscillator approximation vary only modestly between M05-2X and M06-2X but are consistently higher for B3LYP; this reflects the fact that, other than the methyl torsion calculated with B3LYP, harmonic vibrational frequencies are only very slightly dependent on functional (see Supporting Information). When the methyl torsion is treated as a hindered rotor while retaining the harmonic approximation for all other modes, the method for computing DOS influences R_{DOS} in the manner predicted in the previous paragraph: R_{DOS} at high energies is lower when the hindered rotor treatment is added and becomes largely independent of the choice of functional.

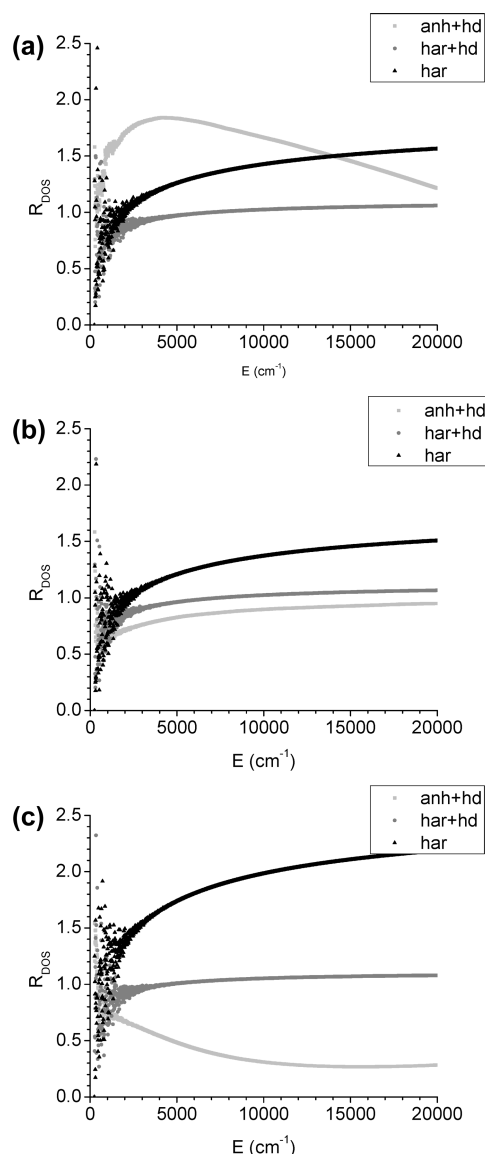


Figure 4. Ratio of the densities of states of cis and trans isomers (R_{DOS}) of the 1-methylallyl radical versus energy above the zero-point energy of the trans isomer: (a) M05-2X, (b) M06-2X; and (c) B3LYP, all with the 6-311+G(2df,2p) basis set. The abbreviations for the method of calculating the densities of states are explained in the caption of Figure 3.

Above about 4000 cm^{-1} , as shown in Figure 4, the harmonic approximation yields a monotonically increasing R_{DOS} for all functionals. Inclusion of anharmonic corrections significantly changes R_{DOS} ; most obviously, the shape of R_{DOS} when the anharmonic approximation is used varies greatly with the functional. For M06-2X, $R_{\text{DOS}}(E)$ increases monotonically and slowly to 0.95 at $20\,000\text{ cm}^{-1}$. In contrast, for M05-2X, $R_{\text{DOS}}(E)$ exhibits a peak value of 1.84 at 4200 cm^{-1} and a subsequent decrease to 1.21 at $20\,000\text{ cm}^{-1}$. $R_{\text{DOS}}(E)$ for B3LYP is concave up with a minimum near $15\,000\text{ cm}^{-1}$.

Absolute values of the densities of states in the energy range $5000\text{--}12\,000\text{ cm}^{-1}$ using the anharmonic treatment are shown in Figure 5a,b for the cis and trans isomers, respectively. The densities of states for each isomer do not depend enormously on the functional, except using B3LYP, where the trans isomer has a higher density of states. This leads to the R_{DOS} being

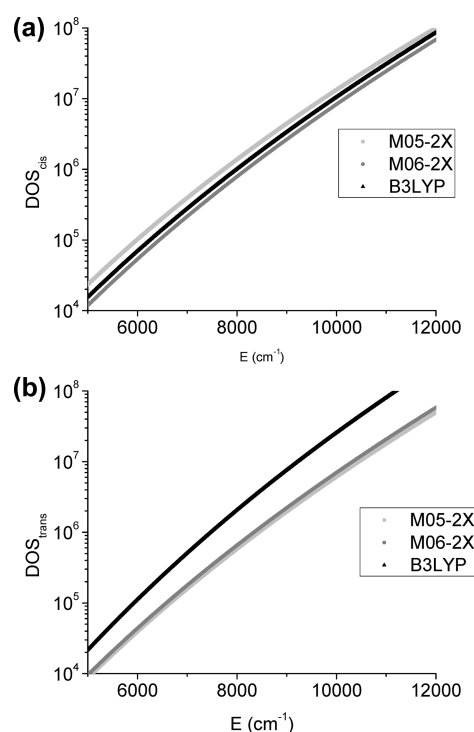


Figure 5. Absolute values of the densities of states for three functionals with the 6-311+G(2df,2p) basis set in the energy range $5000\text{--}12\,000\text{ cm}^{-1}$ above the zero-point energy of the trans isomer. Calculations used the anharmonic treatment of frequencies and a hindered rotor treatment of the methyl torsion to compute densities of states: (a) cis isomer; (b) trans isomer.

much smaller at B3LYP than at M05-2X or M06-2X, as shown in Figure 4.

We now turn to the pressure dependence of the cis:trans ratio of thermalized radicals, with the goal of interpreting these ratios in terms of R_{DOS} . The pressure dependence at 300 K is given in Table 2 and Figure 6. At pressures of 10 atm and lower, little to no pressure dependence is observed. When the pressure is raised to 100 atm, the cis:trans ratio is significantly reduced from the values at lower pressures. The reason for this

Table 2. Population Ratio of Cis to Trans Isomer of the 1-Methylallyl Radical after Quenching at 300 K for an Initial Excitation Energy of 30 kcal/mol (above the Zero-Point Energy of the Trans Isomer)^a

functional	method for DOS	pressure (atm)				
		0.01	0.1	1.0	10.	100.
B3LYP	har	1.59	1.63	1.70	1.69	0.50
	har+hd	0.92	0.91	0.92	0.93	0.40
	anh+hd	0.42	0.39	0.36	0.33	0.12
M05-2X	har	1.41	1.41	1.41	1.42	0.38
	har+hd	1.05	1.05	1.07	1.08	0.33
	anh+hd	1.97	1.93	1.90	1.76	0.54
M06-2X	har	1.54	1.52	1.51	1.57	0.88
	har+hd	1.20	1.19	1.17	1.19	0.75
	anh+hd	1.01	1.00	1.00	1.03	0.72

^aResults for different DFTs and different methods of computing the sums and densities of states. The abbreviations for the method of calculating the densities of states (DOS) are explained in the caption to Table 1.

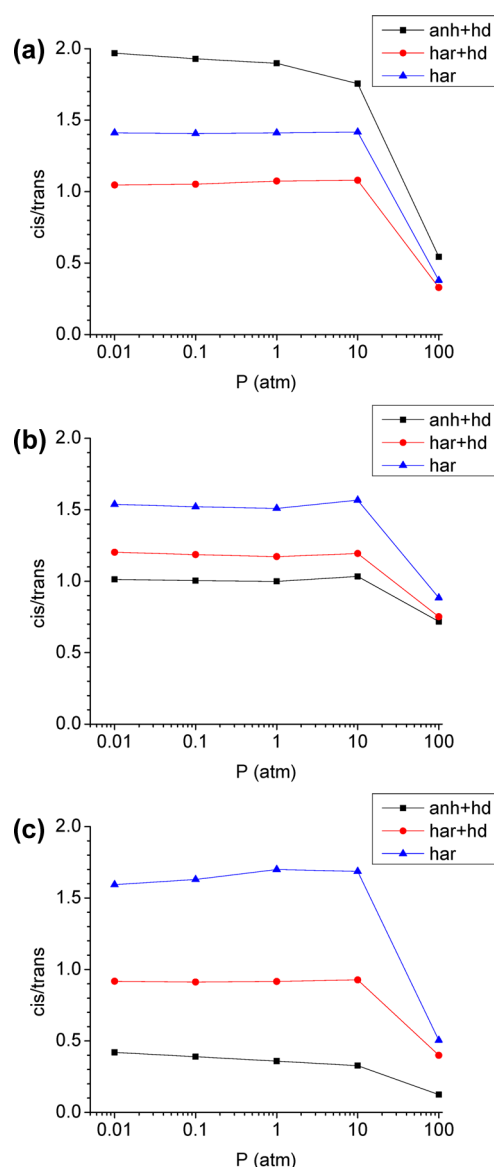


Figure 6. Pressure dependence (in N_2 at 300 K) of the population ratio of quenched 1-methylallyl radicals ($R_{cis:trans}$) formed from chemically activated trans isomer with a thermal distribution of energy shifted upward by 30 kcal/mol ($\sim 10\,500\text{ cm}^{-1}$) from the zero-point energy: (a) M05-2X, (b) M06-2X, and (c) B3LYP, all with 6-311+G(2df,2p) basis set. The abbreviations for the method of calculating the densities of states are explained in the caption of Figure 3.

behavior is clear if we plot the cis:trans ratio of the chemically activated radicals versus time as in Figure 7. Here we only plot one case, using the harmonic oscillator approximation for all modes and the B3LYP functional. This selection exhibits the largest energy dependence of R_{DOS} , so it most clearly illustrates how R_{DOS} controls the cis:trans ratio of thermalized radicals and the pressure dependence thereof. Recall that all simulation results presented here started from 100% trans isomer (cis:trans ratio of zero). At pressures of 10 atm and less, the cis:trans ratio quickly (within ~ 100 ps) reaches a value of 1.7 and then evolves slowly from there to slightly higher values. We hypothesize that this value of ~ 1.7 is a quasi-steady state determined by R_{DOS} . If so, the subsequent evolution corresponds to maintaining this quasi-steady state until

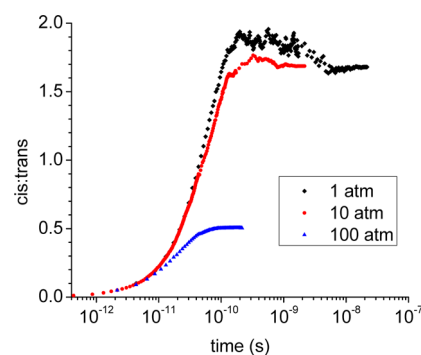


Figure 7. Time history of the population ratio of activated 1-methylallyl radicals ($R_{cis:trans}$) at 300 K and N_2 pressures of 1, 10, and 100 atm. These results are from B3LYP/6-311+G(2df,2p) calculations with a harmonic oscillator treatment of all vibrations (har). Calculations start from the trans isomer at a thermal distribution of energy shifted upward by 30 kcal/mol ($\sim 10\,500\text{ cm}^{-1}$) from the zero-point energy.

quenching reduces the microcanonical rate constant for isomerization below a value that can compete with further quenching. In contrast, at 100 atm, quenching is sufficiently fast that the cis:trans population ratio never rises even as high as one-half of R_{DOS} .

These hypotheses can be confirmed by examining the time evolution of the cis:trans ratio of the chemically activated radicals in energy space, together with R_{DOS} , as in Figure 8. At

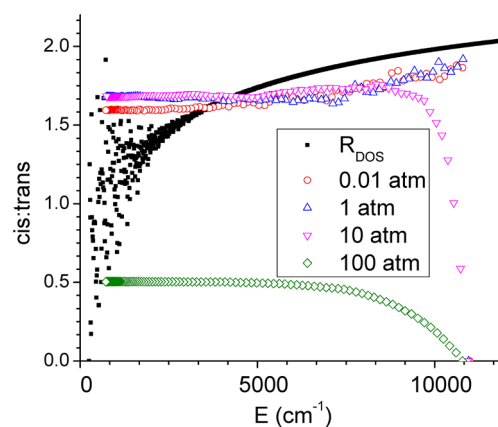


Figure 8. Ratio of densities of states (R_{DOS}) and cis:trans population ratios of chemically activated radicals versus energy (above the zero-point energy of the trans isomer). The population ratios evolve with time as the average energy of the radicals decreases. Calculations start from the chemically activated trans isomer (cis:trans ratio = 0) with a 300 K thermal distribution of energy shifted upward by 30 kcal/mol ($\sim 10\,500\text{ cm}^{-1}$) from the zero-point energy. These results are from B3LYP/6-311+G(2df,2p) calculations with a harmonic oscillator treatment of all vibrations (har). Results are presented for various N_2 pressures.

each pressure, points are plotted at intervals of about 2.5 collisions, so the time interval between points increases by a factor of 10 for each factor of 10 reduction in pressure; at 10 atm the time interval is 22 ps. Starting with the 100 atm results, we see that the energy of the radicals is very rapidly quenched below the activation barrier (in ~ 80 ps) and the population ratio of activated radicals never approaches R_{DOS} . When the pressure is lowered to 10 atm, quenching is slower and the population ratio reaches R_{DOS} before quenching is complete.

Note that at $k(E)$ for the cis \rightarrow trans isomerization is $1.2 \times 10^{10} \text{ s}^{-1}$ at $10\,000 \text{ cm}^{-1}$ but is reduced to $1.2 \times 10^9 \text{ s}^{-1}$ at 6000 cm^{-1} . Each time the pressure is lowered the population ratio follows $R_{\text{DOS}}(E)$ for a longer time. When simulations are carried out using DOS from the B3LYP functional and the harmonic oscillator as in Figure 8, R_{DOS} decreases fairly rapidly with decreasing energy, so the population ratio of quenched radicals is significantly affected by the pressure. It is only necessary to treat the methyl torsion as a hindered rotor to make R_{DOS} much less energy-dependent (Figure 4a) and, therefore, to greatly reduce the difference in computed cis:trans population ratios between 10 and 0.01 atm (Figure 6c and Table 2).

Small alkenes are dominated by their trans isomers, and this has been the focus of most previous studies of internal alkene combustion. The double bonds in fatty acids and their corresponding FAMES are almost entirely cis.¹ The Multiwell simulations discussed above all started from the trans isomer. Multiwell simulations starting from 100% cis isomer yield results essentially identical to those starting from the trans isomer when the bath gas pressure was 1 atm or less. Starting with 100% cis isomer at 100 atm, conversion to trans is of comparable extent to the conversion to cis when starting with the trans isomer.

Recall that previous results assumed a thermal energy distribution shifted upward by 30 kcal/mol from the zero-point energy of the trans isomer; that is, 30 kcal/mol of the ~ 36 kcal/mol available energy partitions to internal energy of the 1-methylallyl radical rather than, e.g., the water molecule coproduct of reaction 1. The true initial energy distribution is not known but probably includes energies well below the barrier to isomerization. Figure 9 shows how varying the initial thermal energy distribution of the trans isomer affects the cis:trans ratio of quenched radicals as a function of temperature (at 1 atm) and pressure (at 300 and 700 K). All three functionals we explored exhibit the same trends, and Figure 9 shows only the results for the M05-2X functional with the anharmonic treatment of vibrations plus hindered rotor treatment of methyl torsion. From Figure 9a one can observe that, when the initial energy deposited in the radicals is 25 kcal/mol or higher, the cis:trans ratio of quenched radicals is 1.9–2.0 regardless of the temperature. At 300 K, we see a large dependence of the population ratio on the initial energy: at 20 kcal/mol the ratio decreases to 1.42, and at 15 kcal/mol the ratio is 0.14. Raising the temperature to only 500 K raises the cis:trans ratio to 1.9 at 20 kcal/mol and to 1.0 at 15 kcal/mol. The pressure dependence at 300 K, shown in Figure 9b, is even more striking, as a pressure dependence exists for all initial energies. At pressures lower than 1 atm, the cis:trans ratio exhibits little pressure dependence for initial energies ≥ 25 kcal/mol. At 1 atm, reducing the initial energy to 20 or 15 kcal/mol lowers the cis:trans ratio significantly. At 100 atm, formation of the cis isomer is negligible at initial energies below 20 kcal/mol. In contrast, at 700 K (Figure 9c) 100 atm pressure cannot fully quench prompt isomerization even at an initial energy of 15 kcal/mol.

This begs the question of what initial energy distribution of the *trans*-1-methylallyl radical will result from reaction 1. We are not aware of any direct experimental or theoretical data that answers this question, but inferences may be drawn from studies of energy partitioning in other heavy–light–heavy (H–L–H) reactions. Experiment and theory for other H–L–H reactions suggest that average translational energy partitioning to reaction products is not insignificant: very roughly 7 kcal/

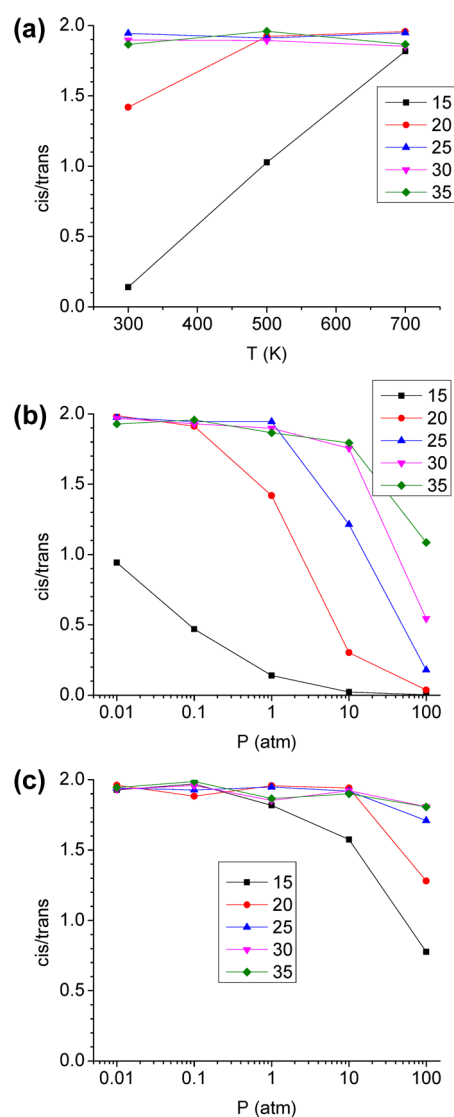


Figure 9. Cis:trans population ratio of quenched 1-methylallyl radicals ($R_{\text{cis:trans}}$) formed from the chemically activated trans isomer possessing a thermal distribution of energy shifted upward by varying amounts from its zero-point energy: (a) temperature dependence at 1 atm of N_2 ; (b) pressure dependence at 300 K; (c) pressure dependence at 700 K. These results are from M05-2X/6-311+G-(2df,2p) calculations with an anharmonic oscillator treatment of vibrations and a hindered rotor treatment of the methyl torsion (anh+hd).

mol.^{52–54} Rotational energy appears modest: perhaps 2–3 kcal/mol.^{54,55} Translational and rotational energy are not expected to be available for isomerization of *trans*-1-methylallyl, regardless of how much initially appears in the radical, but as argued below, the dominant means by which the exothermicity of reaction 1 is made unavailable for prompt isomerization of 1-methylallyl radical is vibrational excitation of the HOH coproduct.

Setser and co-workers measured the vibrational energy distribution of HX ($X = \text{F}, \text{OH}$) formed following reaction of radicals, X, with various organic compounds.^{56,57} In the reaction of OH and F with alkanes at room temperature the extent of HX vibrational excitation was very similar, despite large differences in the available energy: ~ 25 kcal/mol for $X = \text{OH}$ and ~ 40 kcal/mol for $X = \text{F}$. This similarity is due to the

similar underlying dynamics of an H–L–H reaction. This similarity suggests that reaction 1 may be similar to the reaction of F + methylbenzenes to form benzylic radicals, where much of the resonance stabilization of the product radical is unavailable to the HF, presumably due to structural relaxation of the radical in the post-transition state region.⁵⁶ On the basis of the work of Setser and co-workers, much of the HOH product of reaction 1 will be formed with 1–2 quanta of OH stretch (~ 10.5 kcal/mol per quanta), and a significant fraction with 1 quantum of stretch plus one of bend (4.6 kcal/mol). Putting together the above results for all modes, we estimate that the reaction energy unavailable for internal excitation of the *trans*-1-methylallyl radical is most typically 20–30 kcal/mol. Note that *trans*-1-methylallyl radicals will be formed with a wide range of internal excitation, extending from nearly zero to above the energy of the entrance channel. Our use of shifted thermal distributions is not an attempt to mimic the full energy distribution of the nascent radicals, but rather to provide a crude model of subsets of that distribution.

Reaction 5 has a barrier of ~ 1.5 kcal/mol⁵⁸ and an exothermicity of 36 kcal/mol.⁴ From this value and the analyses in the two preceding paragraphs we can estimate the average reaction exothermicity partitioned into internal energy of *trans*-1-methylallyl is typically 7–17 kcal/mol. Figure 9c allows us to predict that at temperatures and pressures relevant to diesel ignition (700 K and pressures up to 100 atm) there will still be extensive formation of the *cis* isomer.

Recall from our discussion of Figure 3 that at temperatures of 900 K, chemically activated isomerization could not be separated from thermal isomerization. This led us to consider the temperature and pressure dependence of the *thermal* rate constant for *trans* \rightarrow *cis* isomerization. The result, calculated using UNIMOL and using the M05-2X functional and a hindered rotor treatment of the methyl torsion, is shown in Figure 10. The rate constant for thermal isomerization can be

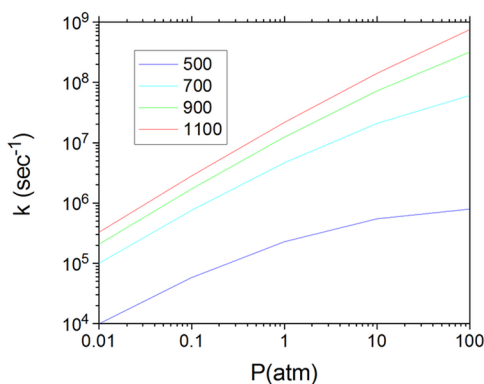


Figure 10. Thermal rate constant for *trans* \rightarrow *cis* isomerization of the 1-methylallyl radical in varying pressures of N₂ bath gas. Calculated using M05-2X/6-311+G(2df,2p) with a harmonic oscillator treatment of vibrations and a hindered rotor treatment of the methyl torsion (har +hd).

compared to the pseudo-first-order rate constant for O₂ addition to 1-methylallyl (reaction 4) under experimental conditions. The overall rate constant for reaction 4 was investigated by Knyazev and Slagle from room temperature to 700 K, although only upper limits to rate constants were obtained at high temperatures.¹³ They found the reaction to have a positive pressure dependence and a negative temper-

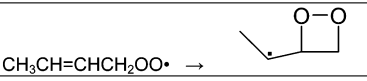
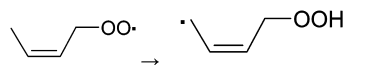
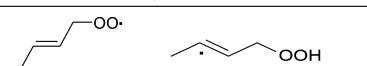
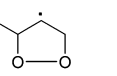
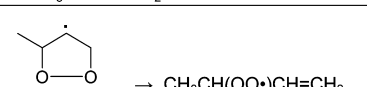
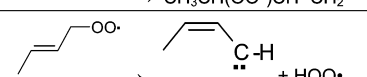
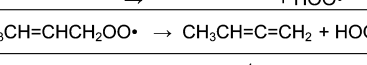
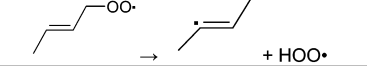
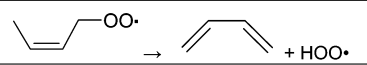
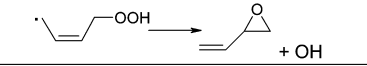
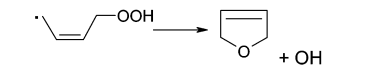
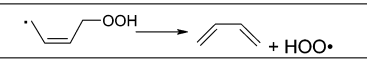
ature dependence. Their results suggest that the reaction is barrierless, which may imply the transition states found for O₂ addition to other allylic radicals are artifacts of the calculations.^{8,14,15} The temperature-dependent rate constant for reaction 4 was taken from the expression of Bounaceur et al. for O₂ addition to allylic radicals, generally $(k(T) = 2.0 \times 10^{-14} e^{+1160/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$.² If we consider air (O₂ mole fraction of 0.21) at 700 K and 10 atm, we obtain a pseudo-first-order rate constant for O₂ addition of $2 \times 10^6 \text{ s}^{-1}$. This pseudo-first-order rate constant is a factor of 10 less than the thermal rate constant for *trans* \rightarrow *cis* isomerization under the same conditions (Figure 10). This means that thermal isomerization of allylic radicals will be important under combustion conditions whether or not they are formed in highly exothermic reactions. This is significant because allylic radicals can also be formed in reactions of alkenes with atomic hydrogen and atomic oxygen,² reactions which are far less exothermic than abstraction by OH radical. Also, larger allylic radicals, especially those formed from FAMES, will have larger thermal energies at a given temperature than the model allylic radical investigated here.

3.2. Fate of the 2-Butene-1-peroxy Radical. Table 3 lists the reaction energies (E_{rxn}) and activation barriers (E_0) for reactions of the *cis* and *trans* isomers of the 2-butene-1-peroxy radical and of the product of the 1,6 H-shift of the *cis* peroxy radical. The potential energy profiles for the *trans* and *cis* isomers are depicted in Figures 11 and 12, respectively. The R–O₂ binding energy (D_0) of the *trans* isomer was computed to be 18.7 kcal/mol at CBS-QB3, which is nearly the same as the calculated value for allylperoxy radical: 19.0 kcal/mol calculated at B3LYP/6-31G(d,p) by Lee and Bozzelli.⁸ The R–O₂ binding energy of the *trans* isomer is 1.0 kcal/mol greater than the *cis* isomer; because the *trans* isomer of the 1-methylallyl radical is 0.0–0.9 kcal/mol lower in energy than the *cis* isomer, the *trans* isomer of the peroxy radical is actually about 1.0–1.9 kcal/mol more stable than the *cis* isomer.

Calculations were applied to a wide range of unimolecular reactions of 2-butene-1-peroxy radical. Some of these transition states likely have significant multireference character that is not treated well at the CBS-QB3 level of theory, and the present results should be regarded as a broad survey of the potential energy profile. Where both *cis* and *trans* isomers undergo the same reaction, the barrier heights and reaction energies are very similar (Table 3). Three reactions have similar barriers of 26–29 kcal/mol: a 1,6 HOO elimination (which only occurs from the *cis* isomer), and cyclization to both four- and five-membered ring compounds. Analogues of the latter two reactions were considered by previous authors at various levels of theory for isobutenyl peroxy or allylperoxy radicals, and our relative energies are quite similar to those found previously.^{8,14,15} Cyclization to a five-membered ring followed by decyclization could, hypothetically, convert the 2-buten-1-peroxy radical to 3-butene-2-peroxy; this class of reactions was first investigated theoretically by Boyd et al.,⁵⁹ and more recently by Olivella and Solé.⁶⁰

A 1,3 HOO elimination from either radical would produce a carbene product and is roughly 78 kcal/mol endothermic (for the triplet state of the carbene). Two reactions are unique to the *trans* isomer. One of these is a 1,5 H-shift from an sp²-hybridized carbon atom that has a barrier about 5 kcal/mol larger than its 20.1 kcal/mol endothermicity. The other is a 1,5 HOO elimination that is over 80 kcal/mol endothermic.

Table 3. CBS-QB3 Activation Barriers (E_0) and Reaction Enthalpies (E_{rxn}) in kcal/mol (at 0 K) of 2-Buten-1-peroxy radical ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet$)^a

reaction	label	E_0		E_{rxn}	
		cis	trans	cis	trans
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet \rightarrow 3\text{-methylallyl} + \text{O}_2$	ROO losing O_2	--	--	17.7	18.7
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet \rightarrow \text{CH}_3\text{CH}=\text{CHCH}=\text{O} + \bullet\text{OH}$	1,3 H-shift	37.0	36.8	-33.2	-34.5
$\text{CH}_3\text{CH}=\text{CHCH}=\text{O} + \bullet\text{OH} \rightarrow \text{CH}_3\text{CH}=\text{CHCH}=\text{O} + \bullet\text{OH}$	hydrogen bond scission	--	--	4.7	4.8
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet \rightarrow \text{CH}_3\text{CH}=\text{C}^\bullet\text{CH}_2\text{OOH}$	1,4 H-shift	36.6	37.7	22.6	23.0
	ROO cyclization to 4-member ring	26.8	28.3	16.9	18.4
	1,6 H-shift	20.9	--	0.8	--
	1,5 H-shift	--	25.0	--	20.1
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet \rightarrow$ 	ROO cyclization to 5-member ring (1,5 cyclization)	29.0	28.9	-0.8	0.9
	decyclization to 3-buten-2-peroxy	26.0	26.0	-2.8	-1.2
	1,3 HOO elimination	<i>b</i>	77.8 ^c	<i>b</i>	78.0 ^c
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet \rightarrow \text{CH}_3\text{CH}=\text{C}=\text{CH}_2 + \text{HOO}^\bullet$	1,4 HOO elimination	39.1	39.2	26.5	28.1
	1,5 HOO elimination	--	<i>b</i>	--	81.8
	1,6 HOO elimination	28.9	--	17.7	--
	QOOH forming 3-member ring (2,4 cyclization)	19.4	--	-4.2	--
	QOOH forming 5-member ring (2,6 cyclization)	26.6	--	-21.5	--
	QOOH losing HOO [•]	25.6	--	17.6	--
	1,6 OH migration	28.8	--	-31.3	--

^aThe trans isomer of $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OO}^\bullet$ is 1.5 kcal/mol lower in energy than the cis isomer. A pair of dashes (--) indicates the reaction is not applicable for that particular isomer. ^bNo transition state was found. ^cTriplet state (slightly) lower in energy than singlet state.

The 1,6 hydrogen shift (reaction 5) of the *cis*-2-buten-1-peroxy radical, which we had hypothesized might compete with O_2 loss, possesses an activation barrier of 20.1 kcal/mol, 4.1 kcal/mol lower than the next lowest barrier of any of the unimolecular reaction considered. This makes it the reaction most likely to compete with loss of O_2 (endothermic by 17.7 kcal/mol). As discussed at the end of the previous section, O_2 addition to 1-methylallyl radical (reaction 4a) is expected to be barrierless, so calculation of the competition between reactions -4a and 5 would require a variational RRKM treatment of O_2 loss from *cis*-2-buten-1-peroxy radical; such a calculation is outside the scope of the present study. Nevertheless, a qualitative analysis provides strong conclusions: barrierless loss of O_2 is expected to have a higher Arrhenius pre-exponential factor (*A*-factor) than formation of the entropically disfavored seven-membered ring of the transition state for 1,6 H-shift. As reaction -4a has a higher *A*-factor and lower barrier than reaction 5, we conclude that, for the 2-buten-1-peroxy radical, the dominant fate of the cis isomer (and the exclusive fate of the trans isomer) is loss of O_2 .

This begs the question: what is the fate of 1-methylallyl radical in combustion chemistry? Potentially, the 1-methylallyl radical may react with other free radicals, including those resonance-stabilized radicals thought to be involved in formation of polycyclic aromatic compounds, and, hence, soot.⁶¹ If there is a cycle of repeated O_2 addition and loss to 1-methylallyl radical, to the extent that a small fraction of *cis*-2-buten-1-peroxy radical undergoes 1,6 H-shift with each cycle, reaction 5 might actually occur to a significant extent. Potentially more important is that such a 1,6 H-shift would have a lower barrier if the methyl group of the reactant was replaced with a larger alkyl (or other) group; however, our calculations⁶² on the 2-pentenylperoxy radical at the same level of theory indicate that the barrier height is only lower by 1.1 kcal/mol than for the 2-buten-1-peroxy radical. Westbrook et al.⁶³ carried out detailed kinetic modeling of the oxidation of FAMES. For the peroxy radicals analogous to the title compound, they found that they could only match experimental ignition delay times if isomerization did not occur. This is

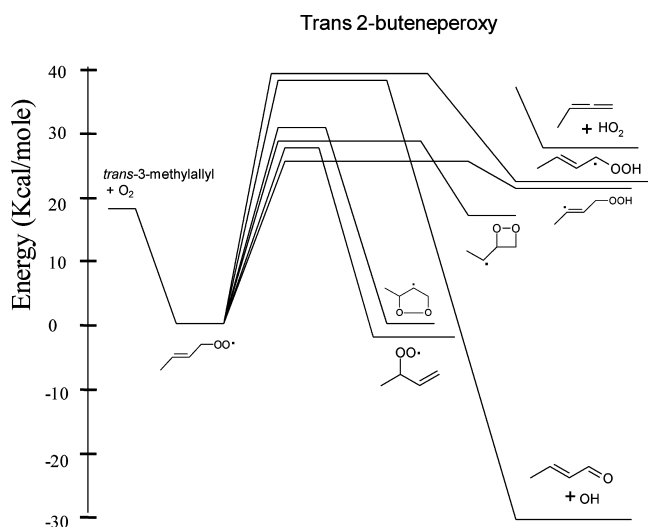
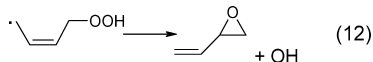


Figure 11. CBS-QB3 potential energy profile for reactions of *trans*-2-butene-1-peroxy radicals (at 0 K).

consistent with the conclusion that dissociation to $R + O_2$ dominates the fate of such radicals.

Let us briefly consider the consequences should reaction 5 occur. Four unimolecular reactions have been identified (Figure 12) for the QOOH product of reaction 5. The lowest barrier process, loss of OH accompanied by cyclization to an oxirane compound:



has a computed barrier of 19.4 kcal/mol (0.6 kcal/mol below the barrier to reaction 5) and is exothermic by 5.0 kcal/mol. This reaction produces two products, so it is effectively irreversible. Other reactions of this QOOH species include cyclization to a five-membered ring, loss of HOO, and 1,6 shift of an OH group. These all have barriers of 25–29 kcal/mol and, therefore, seem unlikely to compete with reactions –5 or

12. Of course, O_2 addition to the QOOH product of (5) may also be important, or even dominant.

4. CONCLUSIONS

This investigation of 1-methylallyl radical formed from $OH + \text{trans-2-butene}$ shows the chemically activated $\text{trans} \rightarrow \text{cis}$ isomerization to be significant under both ambient and combustion conditions. The thermal rate constant for this isomerization may out-compete addition of O_2 to 1-methylallyl for temperatures in excess of 700 K, leading to isomeric scrambling even when the 1-methylallyl is not formed from highly exothermic reactions.

Although the qualitative results summarized above are robust, the exact extent of chemically activated isomerization is highly sensitive to the details of the computational method. This is mainly due to the startling dependence of densities of states (DOS) on methodology. One might have assumed that cancellation of errors would minimize the sensitivity of R_{DOS} to the method used to compute the DOS of these two configurational isomers, but this is not the case. The differences between functionals are not unexpected, and the large effects of treating the methyl rotor as a harmonic oscillator are readily explained. What the authors found most disturbing was that the curvatures of plots of R_{DOS} versus energy changed sign when switching from a harmonic to an anharmonic treatment of the vibrational modes.

The 2-buten-1-peroxy radical, like other allylic peroxy radicals, appears to lose O_2 in preference to further unimolecular reactions. The 1,6 H-shift is the only reaction with the potential to compete to any extent with loss of O_2 . Calculation of the extent to which that will occur would require a variational RRKM calculation of $k(E)$ for loss of O_2 , and preferably, a more accurate theoretical or experimental determination of the barrier height to 1,6 H-shift and the methylallyl- O_2 binding energy.

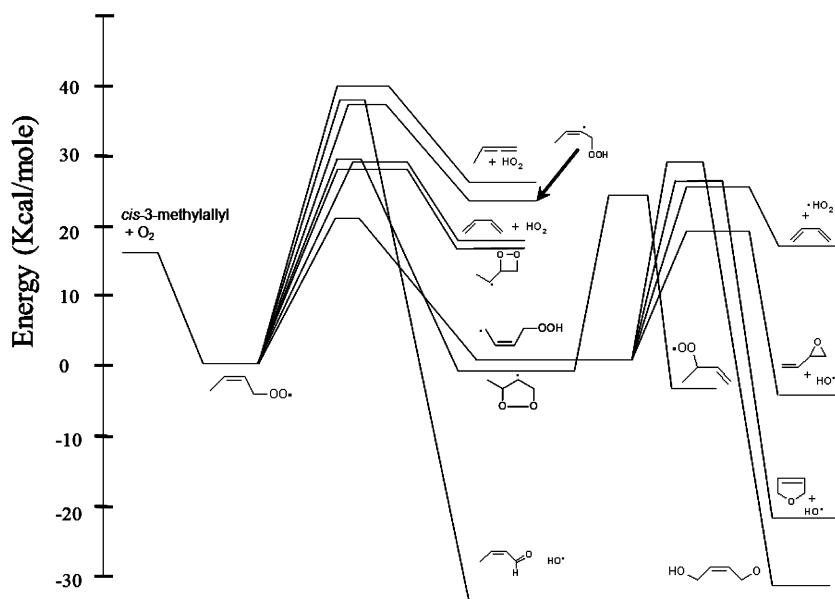


Figure 12. CBS-QB3 potential energy profile for reactions of *cis*-2-butene-1-peroxy radicals (at 0 K).

■ ASSOCIATED CONTENT

■ Supporting Information

Cartesian coordinates, harmonic vibrational frequencies, densities of states, anharmonic constants, and absolute energies of reactants, transition states, and products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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