Oxidation kinetics of n-pentanol: A theoretical study of the reactivity of the 1-hydroxy-1-peroxypentyl radical

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Abstract

n-Pentanol has been considered as a promising alternative fuel for compression-ignition engines due to its potential to reduce greenhouse gases and pollutant emissions. Engine performance is strongly dominated by fuel oxidation chemistry, and thus a more accurate determination of the coefficients of the reactions ruling its oxidation is essential for the utilization of n-pentanol in combustion engines. The reactions involving 1-hydroxy-1-pentyl and molecular oxygen were found to play an important role in controlling the low temperature oxidation chemistry, but have not been investigated experimentally or theoretically; this is also the case for the reactions of the 1-hydroxy-1-peroxypentyl radical, which is formed by the addition of oxygen to the radical center of 1-hydroxy-1-pentyl. This work presents a theoretical study with high level ab initio calculations at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level of theory to shed light on the fate of the 1-hydroxy-1-peroxypentyl radical. The rate coefficients of all the possible intra-molecular hydrogen shift reactions of that radical were computed using variational transition state theory with small

curvature tunneling corrections. For certain reactions, tunneling and variational effects are very pronounced, proving the need for robust methodologies to account for these effects. The hydrogen shift reaction leading to a concerted HO₂ elimination and formation of n-pentanal is the dominant pathway and governs the reactivity of 1-hydroxy-1-peroxypentyl radical at any temperature. The reverse of this reaction was thereby investigated as well. For this prominent pathway, the effects of multistructural (multiple conformers) torsional anharmonicity of the stationary points were taken into account in order to refine the forward and reverse rate coefficients. The rate coefficients calculated at room temperature are compared to those calculated using a previously developed cost-effective multi-conformer transition state theory approach. The system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) theory was used to compute the pressure-dependent rate coefficients, which indicate significant pressure dependence at intermediate and high temperatures. Implementation of the calculated reaction rate coefficients in chemical kinetics models of n-pentanol revealed that our computed rate coefficients enable better insights into the chemistry of n-pentanol, and help to understand how n-pentanal is formed.

Keywords: oxidation, n-pentanol, HO₂ elimination, ab initio, multistructural anharmonicity

1. Introduction

Alcohols have been considered attractive alternatives to conventional petroleum fuels, or as fuel additives, as they can be derived from various renewable feedstocks, and more importantly, possess similar physio-chemical properties to those of fossil fuels [1]. The shorter carbon chain alcohols, i.e. ethanol and butanol isomers, are attractive alternatives to gasoline fuels due to their excellent knock resistance, which allows their application in engines with higher compression ratios and consequently enhances the fuel economy [2, 3]. The pentanol isomers and longer carbon chain alcohols possess stronger reactivity at low temperature conditions and lower knock resistance, so are recognized as suitable alternatives to diesel fuels [4]. The increasing utilization of alternative fuels, such as alcohols, motivates a better understanding of their fundamental combustion kinetics because fuel low-temperature oxidation chemistry plays an important role in advanced engine combustion concepts. This is the reason why, over the last several decades, extensive and intensive efforts have been dedicated to the combustion chemistry of alcohols [1].

Compared to short carbon chain alcohols, n-pentanol and its isomers have several advantages, including higher energy density and favorable physical properties, making them more suitable alternatives and thereby receiving further attention. Their combustion properties have been carefully investigated, with special focus on auto-ignition in rapid compression machines and shock tubes [4-7], laminar flame propagation velocity [8-10], premixed flame structure [11, 12], pyrolysis and oxidation characteristics [13-17]. Consequently, comprehensive chemical kinetics to describe pyrolysis and oxidation chemistry of pentanol isomers have been developed and widely validated against experimental data [4, 5, 10, 14]. Nevertheless, low temperature oxidation chemistry still remains insufficiently understood, as the rate coefficients of certain important pathways in the low temperature oxidation of pentanol isomers have simply been estimated rather than accurately determined [4, 5]. Rate coefficient estimation based on rate rules or analogue reactions might be an efficient and flexible protocol for hydrocarbon species, but for alcohols, the presence of a hydroxyl group in the molecule may make the oxidation chemistry a more complex process [18]. As a matter of fact, special attention has been focused on some important reactions involved in the combustion chemistry of alcohols. For instance, Zádor et al. [19] and Welz et al. [20] investigated ethanol and n-butanol oxidation at low temperatures and pointed out that the reaction associated with the formation of aldehyde and hydroperoxy radical is strongly preferred in low temperature combustion of alcohols. However, to our knowledge, the rate coefficients for the reaction system of fuel radical plus molecular oxygen for n-butanol and n-pentanol have not been studied neither experimentally nor theoretically [3, 4].

The initial step of n-pentanol oxidation is its reaction with radicals such as OH, H or O, which can abstract a hydrogen atom. Based on the Arrhenius parameters for such abstractions, the dominant pathway is abstraction of a hydrogen from the carbon atom connected to the hydroxyl group, leading to the 1-hydroxy-1-pentyl radical [4], as will be shown later. At low and intermediate temperature, this is followed by addition of molecular oxygen to form 1-hydroxy-1-peroxypentyl radical, or a direct reaction between 1-hydroxy-1-pentyl radical and O₂ yielding pentanal and HO₂. In the present work, the fate of the 1-hydroxy-1-peroxypentyl radical and its contribution to the total yield of n-pentanal have been accurately investigated by determining the rate coefficients of the following seven unimolecular reactions in Scheme 1. This allows us to assess its reactivity for the sake of the utilization of n-pentanol (and other alcohols) as an alternative fuel.

We characterized their potential energy surfaces and calculated the rate coefficients with the single-structural variational transition state theory [21] (VTST) including a small curvature tunneling correction as a first approach. Our goal is to elucidate the most prominent pathway among the considered intra-molecular hydrogen shift reactions. Multistructural torsional anharmonicity to account for the effect of the multiple conformers and pressure effects have been estimated to obtain more quantitative results of the prominent pathway, which turned out to be R6 (others can be neglected due to their low rate coefficients). To examine the role of the studied reactions and calculated rate coefficients, we implemented the computed rate coefficients into the chemical kinetic model of n-pentanol by Heufer et al. [4] and carried out simulations on ignition delay times, species concentration profiles and laminar flame speeds.

2. Computational details

2.1 Ab initio calculations

The functional M06-2X [22] with the cc-pVTZ basis set [23] was employed to optimize the geometries and obtain the frequencies of the stationary points of the potential energy surface (PES). Different conformers of each species were automatically generated by the MSTor-2017 code [24] by rotating all the dihedral angles of an optimized geometry by 60 degrees; pseudorotations within the ring of the saddle points were also explored. To refine the energies, a higher level of theory, the CCSD(T) method [25] with the aug-cc-pVTZ basis set [23], was applied to calculate energies using the geometries optimized at the M06-2X/cc-pVTZ level. The electronic structure calculations were carried out using the Gaussian09 package [26].

The minimum energy path (MEP), connecting reactants and products via the corresponding saddle point, was determined with the Gaussrate-2016 code [27] and the Page-McIver method [28] over a reaction coordinate range from -2.2 bohr to +2.2 bohr in mass scaled coordinates using the M06-2X/cc-pVTZ level; a scaling factor obtained with the CCSD(T)/aug-cc-pVTZ level was applied for a further improvement of the MEP. The stepwise increment was set to 0.1 bohr and a mass-scaling factor of 1.0 amu was used. As the region around the saddle point plays the largest role in both the determination of the variational transition state and the contribution from quantum tunneling effects, a smaller stepwise increment of 0.0472 bohr was used between -1.0384 bohr and +1.0384 bohr to

better describe this region. The Hessians were computed every 3 steps. The vibrational frequencies of the modes transverse to the MEP were calculated using a well-defined set of curvilinear internal coordinates, which includes bonds, angles and dihedral angles, and does not yield imaginary frequencies along the MEP. The ground-state vibrational adiabatic potential energy, $V_a^G(s)$, was calculated as follows and further used to calculate the tunneling transmission coefficients using the small-curvature tunneling approach (SCT) [29],

$$V_a^G(s) = V_{\text{MEP}}(s) + \varepsilon^G(s) \quad (1)$$

where s is the reaction coordinate, while $V_{\text{MEP}}(s)$ is the zero point energy exclusive potential energy, defined with respect to that of the reactants, and $\varepsilon^G(s)$ is the local zero point energy, respectively.

2.2 High pressure limit rate coefficient calculations

The high pressure limit rate coefficients of reactions R1-R7 were initially estimated using single structural variational transition state theory [30] with small curvature tunneling corrections [29] and the harmonic oscillator approach (SS-VTST-HO-SCT); the lowest-energy conformers of the reactant and saddle point species at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level were used. The rate coefficients were calculated using the following equation:

$$k_{\text{SS-HO}}^{\text{CVT/SCT}}(T, s) = \kappa^{\text{SCT}} \Gamma \frac{1}{\beta h} \frac{Q_{\text{el}}^{\ddagger}(T) Q_{\text{rovib}}^{\ddagger}(T, s)}{\Phi_t Q_{\text{el}}^{\text{R}}(T) Q_{\text{rovib}}^{\text{R}}(T)} \exp(-\beta V_{\text{MEP}}(s)) \quad (2)$$

where κ^{SCT} is the SCT transmission coefficient, β is $1/k_B T$, k_B is Boltzmann's constant, T is temperature and h is Planck's constant. The factor Γ is the recrossing transmission coefficient, given by the ratio of the CVT rate coefficient to the TST one; CVT and TST stand for canonical variational transition state theory and transition state theory, respectively. Φ_t is the translational partition function per unit volume, Q is the partition function, the superscripts “ $\ddagger$ ” and “R” represent transition state and reactant, respectively, and the subscripts “el” and “rovib” denote electronic and rovibrational (harmonic), respectively. The rate coefficient calculations were performed with Polyrate-2016 code [29]. A scaling factor of 0.955 [31] was used to correct the

vibrational frequencies in order to obtain more accurate partition functions and $V_a^G(s)$ curve and thereby a better description of the torsional anharmonicity and transmission coefficients. As will be presented in Section 3.2, the rate coefficients comparison indicates that, within the whole temperature range we considered, reaction R6 is the prominent one among all the investigated intramolecular hydrogen transfer reactions (R1-R7). Therefore, we refined its rate coefficients by including multistructural torsional anharmonicity effects [32, 33] in the reactant, products and saddle point species to improve both the forward (R6) and reverse (-R6) rate coefficients. The MSTor code [24] was used to compute the necessary multistructural torsional partition functions with coupled torsions, which are defined as follows,

$$Q_{\text{con-rovib}}^{\text{MS-T(C),X}}(T) = \sum_{j=1}^J Q_{\text{rot},j} \exp(-\beta U_j) Q_j^{\text{HO}} \prod_{\eta=1}^t \bar{f}_{j,\eta} \quad (3)$$

where X represents the reactant (R) or the saddle point ($\ddagger$) species of the reaction. The distinguishable structures or conformers of the reactant and saddle point were labeled as $j=1,2,\dots,J$, where J is the total number of conformers and $j=1$ stands for the global minimum-energy conformer. The term U_j represents the potential energy (zero point energy exclusive) of structure j with respect to that of the global minimum. $Q_{\text{rot},j}$ and Q_j^{HO} are the classical rotational and normal-mode harmonic oscillator partition function of conformer j , respectively. The latter is calculated with the following equation,

$$Q_j^{\text{HO}} = \prod_{i=1}^F \frac{\exp(-\beta \hbar \omega_{j,i} / 2)}{1 - \exp(-\beta \hbar \omega_{j,i})} \quad (4)$$

where $\omega_{j,i}$ is the normal mode vibrational frequency of mode i of conformer j , F is the total number of vibrational modes, and $\hbar$ is Planck's constant divided by 2π . $\bar{f}_{j,\eta}$ in Eq. 3 is a factor to include the torsional anharmonicity of the coupled torsion η of the conformer j , and t is the number of coupled torsions. The product of $\bar{f}_{j,\eta}$ is the torsional anharmonicity correction for the coupled torsions, which is based on the coupled torsional potential and is calculated as follows,

$$\prod_{\eta=1}^t \bar{f}_{j,\eta} = (2\pi\beta)^{t/2} \frac{\prod_{m=1}^F \omega_{j,m} \sqrt{\det D_j}}{\prod_{m=1}^{F-t} \omega_{j,m} \prod_{\eta=1}^t M_{j,\eta}} \prod_{\eta=1}^t \exp\left(-\frac{\beta W_{j,\eta}^{(C)}}{2}\right) I_0\left(\frac{\beta W_{j,\eta}^{(C)}}{2}\right) \quad (5)$$

162 where $\bar{\omega}_{j,m}$ are the torsion-projected normal mode frequencies and D_j are the Kilpatrick and
 163 Pitzer torsional moment of inertia matrices, $M_{j,\tau}$ are the local periodicity parameters for
 164 uncoupled torsion τ and I_0 is a modified Bessel function.
 165 The extent of the multistructural anharmonicity of the reactants and saddle point species can be
 166 determined by the ratio of their multistructural torsional partition functions to the single structural
 167 torsional ones (for the global minima), as determined by the following factors $F^{\text{MS-T,R}}$ and $F^{\text{MS-T},\neq}$
 168 for the reactant and saddle points, respectively,

$$F^{\text{MS-T,R}} = \frac{Q_{\text{con-rovib}}^{\text{MS-T(C),R}}}{Q_{\text{con-rovib},j=1}^{\text{SS-T,R}}} \quad (6)$$

$$F^{\text{MS-T},\neq} = \frac{Q_{\text{con-rovib}}^{\text{MS-T(C),\neq}}}{Q_{\text{con-rovib},j=1}^{\text{SS-T},\neq}} \quad (7)$$

169 where $Q_{\text{con-rovib},j=1}^{\text{SS-T,R}}$ and $Q_{\text{con-rovib},j=1}^{\text{SS-T},\neq}$ are the single structural rovibrational partition functions with
 170 torsional anharmonicity corrections for the lowest energy structures of reactant and saddle points,
 171 respectively. The multistructural anharmonicity effect on the overall reaction can be measured as

$$F^{\text{MS-T}} = \frac{F^{\text{MS-T},\neq}}{F^{\text{MS-T,R}}} \quad (8)$$

172 Finally, the rate coefficients including multistructural, torsional and variational effects, as well as
 173 SCT corrections, labeled as MS-T-VTST-SCT, are calculated as

$$k^{\text{MS-T(C)/SCT}}(T,s) = \kappa^{\text{SCT}} \Gamma \frac{1}{\beta h} \frac{Q_{\text{el}}^{\neq} Q_{\text{con-rovib}}^{\text{MS-T(C),\neq}}}{Q_{\text{el}}^{\text{R}} Q_{\text{con-rovib}}^{\text{MS-T(C),R}}} \exp(-\beta V^{\neq}) \quad (9)$$

174 The SS-HO and MS-T rate coefficients at 298.15 K calculated as outlined above are compared to
 175 those calculated using the cost-effective multi-conformer transition state theory [34] (MC-TST, Eq.
 176 10) approach previously developed for peroxy radical H-shift reactions under atmospheric
 177 conditions for R2-R6 (Table S1 in supplementary material) [35]. This represents a cost-effective
 178 alternative which is more feasible and practical for large systems with many conformers, like the
 179 one addressed in the present work, and has continuously yielded rate coefficients within a factor of

five of experimental results [36-39]. The MC-TST rate coefficients, $k^{\text{MC-TST}}$, are calculated as:

$$k^{\text{MC-TST}} = \kappa^{\text{Eckart}} \frac{1}{\beta h} \frac{\sum_i^{\text{S}} \exp(-\beta \Delta E_i) Q_i^{\text{HO}}}{\sum_j^{\text{R}} \exp(-\beta \Delta E_j) Q_j^{\text{HO}}} \exp(-\beta(E_{\text{SP}} - E_{\text{R}})) \quad (10)$$

κ^{Eckart} is the Eckart tunneling coefficient [40] and the two sums run over the conformers of the saddle point and reactant species, and include only conformers within 2 kcal/mol in electronic energy of the lowest-energy conformer at the B3LYP/6-31+G(d) level. ΔE is the zero-point energy of a given saddle point or reactant conformer calculated relative to the corresponding lowest-energy conformer. The reaction barrier ($E_{\text{SP}} - E_{\text{R}}$) is the difference in energy between the lowest-energy saddle point and reactant conformers. The reaction barrier is calculated using electronic energies at the CCSD(T)-F12a/VDZ-F12// ω B97X-D/aug-cc-pVTZ level in Molpro 2012 with a ω B97X-D/aug-cc-pVTZ zero-point vibrational energy correction calculated in Gaussian 09 [41-44]. The relative conformer energies ΔE and partition functions Q are calculated at the ω B97X-D/aug-cc-pVTZ level. A full description of this approach is given elsewhere [35].

2.3 Pressure dependent rate coefficients calculations

The Hinshelwood-Lindemann mechanism for unimolecular reactions, as implemented in the system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) utility code [45], was used to estimate pressure effects within a wide pressure range. This mechanism uses the modified strong collision model to calculate the de-energization rate coefficient of the activated reactant, k_c .

Although there are more robust methodologies to estimate pressure effects, such as the quantum-Rice-Ramsperger-Kassel-Marcus (QRRKM) theory with master equation analysis [46], SS-QRRK allows the user to introduce multi-structural anharmonicity effects. These effects can be very pronounced, making the SS-QRRK method a good choice to estimate pressure effects in those cases.

We used nitrogen as bath gas, with a de-energization temperature dependence for the calculations given by the form $\langle E \rangle_{\text{down}} = 200(T/300)^{0.85} \text{ cm}^{-1}$ [47], its Lennard-Jones parameters are

$\sigma = 3.798 \text{ \AA}$ and $\varepsilon/k_{\text{B}} = 71.4 \text{ K}$ [48]. For the radical 1-hydroxy-1-peroxypentyl, the Lennard-Jones parameters are not available, so we used those of n-pentanol as an approximation, as both

molecules have a hydroxyl group. The parameters of n-pentanol are $\sigma = 5.649 \text{ \AA}^0$ and $\varepsilon/k_B = 524.2 \text{ K}$, respectively.

However, we have recently showed that the SS-QRRK utility code does not accurately determine the thermal fraction of unimolecular states above the threshold energy, F_E , in systems with more than around eight atoms at high temperatures, as a consequence of an unphysical underestimation of the collision efficiency parameter β_c , thereby underestimating the low pressure rate coefficients at high temperatures [49]. In that work, an alternative definition was implemented for β_c , which yields more accurate F_E values and thereby fixes the underestimation of the low pressure rate coefficients at high temperatures; the parameter β_c is used to determine k_c , suggesting the need for an accurate estimation of that parameter in the low pressure rate coefficients calculations. More details regarding these calculations can be found elsewhere [49].

2.4 Numerical simulations of n-pentanol oxidation

We updated the kinetic model of n-pentanol oxidation proposed by Heufer et al. [4] (hereafter referred to as the original model) using the calculated rate coefficients and thermochemical properties in the present work, and obtained what we call the updated model. In the original model, the rate coefficients of some of the studied reactions (R2-R4 and R7) were estimated based on the rate rules established for alkanes [50] and alcohols [3]. As mentioned previously, such a method is simple and flexible to obtain a rough understanding of combustion chemistry, but large uncertainties are expected to lie in the reaction rate coefficients and branching ratios of the studied reaction pathways. In the updated model, the forward and reverse calculated rate coefficients were implemented as three parameter Arrhenius-type expressions, together with the NASA polynomials calculated for the 1-hydroxy-1-peroxypentyl species. Rate coefficients in three parameter Arrhenius-type and NASA polynomials can be found in the supplementary material (Tables S6 and S7, respectively). Since reactions R1, R5 and R6 were not considered in the original model, thermochemistry and transport properties of some species involved in these three reactions were missing, and thus we used those of species having similar chemical structures in our updated model;

however, as will be discussed later, two of these reactions did not play an important role in the investigated oxidation process.

Ignition delay time simulations were performed under closed homogeneous batch reactor at constant volume conditions (CONV) and variable volume conditions accounting for facility effects (VARV). Simulations were compared to the predictions of the original model and to experimental data collected from rapid compression machine (RCM) and shock tube (ST) experiments [6]. Initial pressures were 9 bar, 19 bar and 30 bar, and temperatures were within the 650-1250 K range; the equivalence ratio of the n-pentanol/air mixture was 1.0, as used in Heufer et al.'s previous study [6]. According to the description of Heufer et al. [6], the uncertainty of experimentally measured ignition delay times in RCM and ST was estimated to be 10% [51] and 15% [52], respectively.

The oxidation of n-pentanol was simulated in a perfectly stirred reactor at a pressure of 10 atm, a residence time of 0.7 s and using three equivalence ratios of 0.5, 1.0 and 2.0; it was compared to the experimental data reported by Togbé et al. [16]. The transient solver has been applied to obtain the steady-state solutions at each temperature.

The laminar flame speeds as a function of the equivalence ratio were predicted and compared with the measurements from Nativel et al. [8] at atmospheric pressure and three initial temperatures of 353 K, 423 K and 473 K. The flame speed is sensitive to the oxidizer composition; therefore, for the comparison, we used the 20.9% O₂ + 79.1% N₂ mixture, that is, the one used by Nativel et al. [8]. The simulations were performed with the Chemkin-Pro 15131 software [33].

3. Results and discussion

3.1 Topology of the potential energy surface

The CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ energy profiles with the global minimum conformers for reactions R1-R7 are shown in Figure 1, together with the energies calculated at the M06-2X/cc-pVTZ level. The names and structures, along with the energies (zero point exclusive) of the minimum (reactants, products and intermediate complexes) and saddle point species on the PESs of the investigated reactions are listed in Table 1 and Table 2, respectively. The T1 diagnostic values are less than 0.02, except for the HO₂ radical and SP1, both of which are less than or around 0.04, indicating that the energies calculated by the single reference method should be reliable [53]. The barrier heights computed at the lower level of theory are in good agreement with those at the

higher level, with a maximum deviation of 1.43 kcal/mol for the saddle point of R2. Comparison of the barrier heights suggests that the intramolecular hydrogen shift and concerted HO₂ elimination that yields n-pentanal as co-product (R6) is the most energetically favored reaction among all the studied reactions, with the lowest barrier height, 15.45 kcal/mol (zero point energy exclusive). A hydrogen-bonded intermediate complex between the incipient n-pentanal and HO₂ species can be formed in the exit channel of the PES; this complex would dissociate to form the final products with a barrier height of around 10 kcal/mol. The other reaction channels (R1-R5 and R7) are not competitive due to their much higher barrier heights, especially at low and intermediate temperatures when the rate coefficients are more sensitive to the barrier height. In particular, the intramolecular hydrogen shift and concerted HO₂ elimination leading to 1-penten-1-ol (R7) and the isomerization to form 1-hydroxy-1-hydroperoxy-2-pentyl (R2) are the least competitive reaction channels, with barrier heights of 36.96 and 35.45 kcal/mol, respectively.

Table 1. Reactant, products and intermediate complex species on the PESs of the studied reactions

#	Species name	Structure	Relative energy ^a
α -ROO	1-hydroxy-1-peroxypentyl		0.00
α -QOOH-O	1-hydroperoxy-1-pentoxy		20.40, (20.58) _b
α -QOOH-2	1-hydroxy-1-hydroperoxy-2-pentyl		(15.14) _b
α -QOOH-3	1-hydroxy-1-hydroperoxy-3-pentyl		14.50, (14.32) _b
α -QOOH-4	1-hydroxy-1-hydroperoxy-4-pentyl		14.20, (17.34) _b
α -QOOH-5	1-hydroxy-1-hydroperoxy-5-pentyl		16.71, (14.32) _b
Complex	n-pentanal...HO ₂ complex		8.84, (9.79) _b
α -P1	n-pentanal + HO ₂		18.63, (22.14) _b
α -P2	1-penten-1-ol + HO ₂		28.21, (30.21) _b

^a Zero point energy exclusive obtained at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level, in kcal/mol and relative to that of the α -ROO reactant. Global minimum conformers of each species were used. For the species α -QOOH-2, we experienced convergence issues with the CCSD(T)

method

^b The values shown in parentheses are obtained at the M06-2X/cc-pVTZ level

Table 2. Saddle point species on the PESs of the studied reactions

#	Reactions	Relative energy ^a
SP1	α -ROO $\leftrightarrow$ α -QOOH-O (R1)	26.51
SP2	α -ROO $\leftrightarrow$ α -QOOH-2 (R2)	36.96
SP3	α -ROO $\leftrightarrow$ α -QOOH-3 (R3)	27.59
SP4	α -ROO $\leftrightarrow$ α -QOOH-4 (R4)	25.41
SP5	α -ROO $\leftrightarrow$ α -QOOH-5 (R5)	28.72
SP6	α -ROO $\leftrightarrow$ n-pentanal + HO ₂ (R6)	15.45
SP7	α -ROO $\leftrightarrow$ 1-penten-1-ol + HO ₂ (R7)	35.54

^a Zero point energy exclusive obtained at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level, in kcal/mol and relative to that of the α -ROO reactant. Global minimum conformers of each species were used

The barrier heights are strongly dependent on the ring strain of the saddle points. Commonly, the isomerization of the peroxy radical via 6-, 7- and 8-membered rings (1,5; 1,6 and 1,7 H-shifts, respectively) to form a hydroperoxy alkyl radical are the most energetically favored pathways in large alkyl radicals, while the isomerization via a 5-membered ring saddle point (1,4 H-shift) usually has the most pronounced ring strain and is the least favored [18, 36, 54]. Nevertheless, as the α -ROO radical in alcohols has a hydroxyl group near the radical center, the concerted HO₂ elimination yielding aldehyde as the co-product via a 5-membered ring saddle point (R6) exhibits the lowest reaction barrier height; similar results have been observed for the combustion of ethanol [2] and n-butanol [20] (See Table 3).

Table 3 summarizes the zero point energy inclusive barriers for the reactions of α -ROO radical from C1-C5 alcohols and n-pentane reported in literature and the present study. Despite using different levels of theory and basis sets, the barrier heights for each type of reaction reported by different authors are in good agreement. The barrier heights of the HO₂ elimination reaction forming

corresponding aldehydes for different alcohols are similar and lower than the barriers for the other competing unimolecular reactions, highlighting the importance of this type of reaction in the combustion of alcohols. Meanwhile, the 5-membered ring isomerization (1,4 H-shift) to form an α -QOOH-2 radical and the concerted elimination reactions forming olefin or enol show the highest barrier heights, probably due to the large ring strain [18, 55].

From the comparison provided in Table 3, it can be inferred that the calculated barrier heights are very sensitive to the level of theory employed. We have used a high level of theory to accurately determine this parameter, as it is well known that rate coefficients are sensitive to the barrier height. For the reactions other than reactions R6 and –R6, neglecting multi-structural anharmonicity likely increases the uncertainty by yielding certain overestimation in their rate coefficients. These might be the most important sources of uncertainty in our calculations, and might affect our predictions on the yield of n-pentanal, but higher levels of theory are not feasible for this reactive system with 8 non-hydrogen atoms.

313 Table 3. Comparison of zero-point energy inclusive barriers for the reactions in different α -ROO

Reactions	Reaction type	methanol	ethanol		n-butanol		n-pentanol		n-pentane
α -ROO $\leftrightarrow$ α -QOOH-O	1,4OH H-shift	46.2	23.4	21.8	22.2	22.0	<i>N/A</i>	23.4	-
α -ROO $\leftrightarrow$ α -QOOH-2	1,4 H-shift	-	37.6	36.5	31.8	32.7	34.7	33.4	34.6
α -ROO $\leftrightarrow$ α -QOOH-3	1,5 H-shift	-	-	-	22.5	23.6	23.9	23.9	22.8
α -ROO $\leftrightarrow$ α -QOOH-4	1,6 H-shift	-	-	-	23.9	24.7	23.4	21.8	25.8
α -ROO $\leftrightarrow$ α -QOOH-5	1,7 H-shift	-	-	-	-	-	<i>N/A</i>	25.2	<i>N/A</i>
α -ROO $\leftrightarrow$ aldehyde + HO ₂	Concerted 1,4 OH H-shift and HO ₂ -loss	12.9	12.5	11.4	12.8	12.4	14.1	12.3	-
α -ROO $\leftrightarrow$ enol* + HO ₂	Concerted 1,4 H-shift and HO ₂ -loss	-	32.0	30.4	32.3	32.3	32.5	31.7	31.1
Ref		[56] ^a	[19] ^b	[2] ^c	[20] ^d	[20] ^e	[57] ^f	this study ^g	[57] ^e

314 * The product is olefin (1-pentene) for n-pentane.

315 - These reactions do not exist for the specified fuel.

316 *N/A* These data have not been computed.

317 ^a Computed at the CCSD(T)/cc-pVTZ//CASSCF/6-311G(d,p) level.

318 ^b Computed with the RQCISD(T) method and the cc-pVTZ and cc-pVQZ basis sets using the geometries obtained at the B3LYP/6-311++G(d,p) level, and extrapolated
319 to the infinite basis set cc-pV ∞ Z.

320 ^c Computed with the G3B3 method using the geometries obtained at the B3LYP/6-31G(d) level.

321 *d* Computed with the CBS/QB3 method using the geometries obtained at the B3LYP/6-311++G(d,p) level.

322 *e* Computed with the RQCISD(T) method and the cc-pVDZ and cc-pVTZ basis sets using the geometries obtained at the B3LYP/6-311++G(d,p) level, and extrapolated

323 to the infinite basis set cc-pV ∞ Z.

324 *f* Computed with the G4 method using the geometries obtained at the B3LYP/6-31G(2df,p) level.

325 *g* Computed at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level using the global minimum conformers; zero-point energies are scaled by a factor of 0.955

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3.2 High pressure limit rate coefficients

The SCT transmission coefficients accounting for quantum tunneling are depicted in Figure 2 as a function of temperature. Tunneling is more pronounced in reaction R1, even though this reaction does not have the highest barrier height, reaching an order of magnitude of 10^{12} at 200 K; this is due to the larger curvature of the reaction path, as a hydrogen atom is being transferred between two oxygen atoms. The reaction showing the lowest tunneling contribution is R6, with a transmission coefficient value of 1.63 at 200 K; this is due to its low barrier height compared to the other reactions. We conclude that tunneling plays an important role in the intramolecular hydrogen shift reactions R1-R5, especially at low to intermediate temperatures, but this effect is modest in the concerted HO₂ elimination reactions R6 and R7.

The high pressure limit rate coefficients of the studied reactions calculated using the SS-VTST-HO-SCT method over a broad temperature range from 200 K to 3000 K, are plotted in Figure 3; the tabulated rate coefficients can be found in the supplementary material (Table S3). All the rate coefficients exhibit a positive temperature dependence, i.e. increasing with increasing temperature. At lower temperatures, the rate coefficients are highly sensitive to the barrier heights and larger differences are observed between the different reactions. It is noteworthy that the concerted HO₂ elimination reaction with simultaneous formation of n-pentanal (R6) is the fastest reaction across the studied temperature range; its rate coefficients are several orders of magnitude larger than those of the other reactions, which is due to its low reaction barrier as shown in Figure 1. This observation is in agreement with the previous findings reported by da Silva et al. [2] for the 1-hydroxy-1-peroxyethyl radical, highlighting the prominent role of the concerted HO₂ elimination reaction in alcohol combustion chemistry.

However, in a previous work by Heufer et al. [4], it was found that the concerted HO₂ elimination reaction was triggered by a direct reaction between the 1-hydroxy-1-pentyl radical and molecular oxygen that yields n-pentanal and HO₂ as well, as opposed to the stepwise reaction sequence suggested in the present study. The direct reaction, which is implemented by Heufer et al. [4] using the corresponding reaction in ethanol oxidation [2] as analogy, involves the formation of an activated intermediate, and would be important at low pressure and high temperature conditions at

which the 1-hydroxy-1-peroxypentyl intermediate radical is less prone to be stabilized. On the other hand, the stepwise reactions studied here involve stabilization of the 1-hydroxy-1-peroxypentyl radical formed by O₂-addition to 1-hydroxy-1-pentyl and a subsequent concerted elimination reaction forming n-pentanal and HO₂. Both mechanisms, direct and stepwise, are important to describe the overall process and the yield of n-pentanal, and their competition remains interesting for future investigations. Our calculated rate coefficients help to shed light into this matter, as will be discussed later in Section 3.5.

Recalling the barrier heights given in Figure 1, R2 and R7 have much higher barrier heights and, correspondingly, they exhibit the lowest rate coefficients; R1, R3, R4 and R5 share comparative barrier heights and thus similar rate coefficients. These reactions become more competitive as temperature increases due to their positive temperature dependence and the smaller sensitivity of the rate coefficients to the barrier height in the high temperature regime. Still, even at 3000 K, R6 has the largest rate coefficient by about an order of magnitude.

In addition, our calculated rate coefficients for reactions R2-R4 and R7 are compared to those used in the original model by Heufer et al. [4] in Figure S1, but reactions R1, R5 and R6 were not implemented in the original model, so this comparison is not possible.

Given the prominence of R6 over the other reactions, the MS-T-VTST-SCT method was applied to account for the effects of the multiple conformers and torsional anharmonicity of the involved species to determine the high pressure limit rate coefficient more accurately. The reverse reaction of R6 (-R6) has a submerged barrier of -3.18 kcal/mol relative to the separate pentanal and HO₂ species, and is expected to be important as well; therefore, its rate coefficients were also determined using both the SS-VTST-HO-SCT and MS-T-VTST-SCT methods. However, this reaction is a bimolecular reaction and the reaction rate thus depends on the concentration of the bimolecular reaction partner HO₂, which is important in both combustion and atmospheric chemistry. The multistructural anharmonicity effect on the overall reactions R6 and -R6, as defined by the factor $F^{\text{MS-T}}$ in Eq. 8, is plotted in Figure 4. Multistructural anharmonicity hinders reactivity within the whole temperature range we considered, as the values of $F^{\text{MS-T}}$ are lower than 1. This is due to the larger number of conformers for the reactant species compared to the saddle point species, as the cyclic structure in the latter hinders conformational flexibility. For the forward reaction R6, the

multistructural factor monotonically decreases with the increase of temperature. In contrast, for the reverse reaction -R6, the multistructural factor shows a monotonically increasing trend with temperature.

The final high pressure limit MS-T-VTST-SCT rate coefficients of reactions R6 and -R6 are shown in Figure 5 and tabulated in Table S4, together with those calculated with the SS-VTST-HO-SCT method for comparison purposes. As shown in Figure 5, neglecting multistructural torsional anharmonicity (SS-VTST-HO-SCT method) would lead to a significant overestimation (up to a factor of five) of the rate coefficients at intermediate and high temperatures; this is mainly due to the contribution of the large number of conformers of the reactants/products (314 and 45 distinguishable conformers for 1-hydroxy-1-peroxypentyl and n-pentanal, respectively), which become more important when temperature is increased, as the saddle point has a limited number of conformers (24 distinguishable conformers). These findings support the methods we chose for our kinetic study; as we already discussed, using a different methodology would miss multi-structural anharmonicity, leading to large errors in the calculated rate coefficients.

The rate coefficients of reaction -R6 exhibit a non-Arrhenius behavior, with a negative temperature dependence at temperatures below 800 K (negative activation energy); at higher temperatures the opposite trend is found, with a positive temperature dependence (positive activation energy), which results in a minimum at around 800 K. This behavior is the result of the presence of a submerged barrier, which induces a change in the sign of the activation energy with temperature, and has been observed in other reactions with submerged barriers and pre-reactive intermediate complexes [58, 59]. These results suggest that the recombination of n-pentanal and HO₂ radical becomes important at lower temperatures, and may have to be considered in the atmospheric oxidation of n-pentanol due to its large rate coefficient. This is in line with modeling studies based on calculations for the atmospherically important oxidation of acetaldehyde and acetone, which suggest that in the upper part of the troposphere in certain regions, the addition of HO₂ may be an important sink of those species [60, 61].

Finally, it should be highlighted that variational effects were found to be important at low temperatures in reactions R6 and -R6, indicating the need of using the variational formulation of the

transition state theory to accurately address the kinetics of this kind of reactions; this effect is negligible at intermediate and high temperatures though. For instance, at 200 K and 500 K, the ratios of the non-variational rate coefficient to the variational one in reaction R6 are 2.36 and 1.38, respectively.

Figure 6 shows a comparison between the rate coefficients of the reaction α -ROO $\rightarrow$ aldehyde $\cdots$ HO₂ for ethanol calculated by da Silva et al. [2] using the G3B3 composite theoretical method, where aldehyde $\cdots$ HO₂ is an intermediate complex formed by the incipient products, and those for n-pentanol calculated in the present work. The rate coefficients for ethanol are larger than those for n-pentanol. At low temperatures or atmospheric conditions, the differences are significant, with a ratio between the rate coefficients of up to 22. At higher temperatures, differences are reduced and might be within the error of calculations. This finding highlights the importance of calculating rate coefficients for these processes to prevent the use of analogue reactions as they may lead to wrong predictions in kinetic modeling, especially in the low temperature regime (atmospheric chemistry). The rate coefficients provided in the present study are useful to update chemical kinetic models for n-pentanol, as well as those for larger alcohols consisting of analogue reactions whose rate constants are not computationally feasible.

The high pressure limit rate coefficient at 298.15 K calculated with the MS-T-VTST-SCT approach for R6 is compared to that calculated using the cost-effective MC-TST approach developed by Møller et al. [35] for peroxy radical H-shifts under atmospheric conditions (Table S1). Compared to the MC-TST rate coefficients, which include neither variational nor torsional anharmonicity effects, using the less sophisticated Eckart approach for tunneling and neglecting those conformers above a 2 kcal/mol energy cut-off, $k^{\text{MS-T-VTST-SCT}}$ rate coefficient is smaller by a factor of 10.8. The differences between these two theoretical approaches cannot be attributed to a single source, but highlight the challenges of calculating accurate reaction rate coefficients for reactions involving species with numerous conformers. Differences in the barrier heights calculated at the two levels of theory likely represent the largest source of difference between the two approaches. Variational effects, which are not included in the MC-TST approach, might also contribute to the differences between the two sets of rate coefficients.

3.3 Pressure dependent rate coefficients

In practical combustion facilities, pressure is usually less than the high-pressure limit; we therefore estimated pressure effects for the reaction R6 using the SS-QRRK method [45] with a recently developed scheme by three of us [49], as was previously explained. Rate coefficients at various temperatures and pressures are given in Figure 7 and tabulated in Table S5. The high pressure limit is essentially achieved at around 1000 atm. For atmospheric implications, pressure is not an issue as its effect in the rate coefficients is negligible at temperatures below 375 K. However, within the temperature range of interests in combustion, that is, above 500 K, pressure effects must be considered as they significantly reduce the value of the rate coefficients.

3.4 Role of the calculated rate coefficients in n-pentanol oxidation chemistry

The performance of the original model of Heufer et al. [4] and the updated model including the rate coefficients calculated here are examined by comparing them against the experimentally measured ignition delay times [6], species concentration profiles [16] and laminar flame speeds [8] of n-pentanol oxidation reported in the literature.

Due to the multi-well nature of the considered PES, the approach to implement our calculated rate coefficients for reactions R1-R7 requires further clarifications. Both the original and updated model include formation of the different possible 1-hydroxy-pentyl and 1-hydroxy-peroxypentyl radicals and some subsequent reactions, but in the updated model we also include our calculated rate coefficients for reactions R1-R7. Our focus on the reactions of the 1-hydroxy-1-peroxypentyl radical is due to the fact that this is by far the dominant one and its formation is kinetically favored, indicated by the Arrhenius parameters for hydrogen abstraction reactions from different carbon sites of n-pentanol as well as for those for the subsequent oxygen addition reactions.

In Figure 8, we show some reactions that determine the yield and fate of the different hydroxy-peroxypentyl radicals that can be formed from n-pentanol. Species and reactions highlighted by green arrows and squares are the most prominent ones, supporting the methodology we used in this work. The first step, that is, hydrogen abstraction from n-pentanol, mainly produces 1-hydroxy-1-

pentyl radical as this is the most kinetically favored pathway according to the Arrhenius parameters implemented in the kinetic model for the hydrogen abstraction from different C sites by O₂, HO₂, OH and so on. For instance, the rate coefficients implemented in the model for the hydrogen abstraction by OH from C1 site of n-pentanol (forming 1-hydroxy-1-pentyl radical) are at least 3.5 times larger than those for abstraction from C2 site, which is the second most kinetically favored pathway within the 500-2000 K temperature range.

Regarding the second step, i.e. O₂ addition, one could therefore expect a favorable ratio for 1-hydroxy-1-peroxypentyl radical via addition into the C1 site, enhancing the role of the reactions we investigated, which are those featured in the chart as the third step. This O₂ addition reaction competes with the direct reaction of 1-hydroxy-1-pentyl radical and O₂ that yields n-pentanal and HO₂ (dashed arrow), which is also implemented in both kinetic models.

Finally, among the different reactions featured in the third step, it can be inferred that reaction R6 (green arrow) vastly dominates the fate of 1-hydroxy-1-peroxypropyl radical at any temperature and pressure (as proved by our detailed kinetic study). This would hinder other competing reactions, such as the formation of cyclic ethers from 1-hydroxy-1-peroxy-2-pentyl, 1-hydroxy-1-peroxy-3-pentyl, 1-hydroxy-1-peroxy-4-pentyl, and 1-hydroxy-1-peroxy-5-pentyl radicals, which are also included in both kinetic models.

Our working assumption has been further supported by additional jet stirred reactor simulations, which show that 1-hydroxy-1-pentyl and 1-hydroxy-1-peroxypentyl radicals appear in much higher concentrations than the other isomeric radicals, as described in the supplementary material (Figure S2). These findings support our study of a single but dominant reaction (R6) as part of the multi-well PES, which also includes the important effects of the multiple conformers of reactants and saddle point. The reactivity of the other radical isomers has not been modified relative to the original model. The reader is referred to the original kinetic model [4] for additional insights into the rest of the reactions that constitute the multi-well PES of the investigated reactive system as well as for their Arrhenius parameters.

Figure 9 compares the ignition delay times predicted by the original model and the updated model at 9 bar, with (VARV) and without (CONV) facility effects; both the measurements in RCM and ST are plotted. Overall, the updated model with facility effects (VARV-updated) is able to slightly better

reproduce the experimental data at low and intermediate temperatures (625 K to 1000 K) and the negative temperature coefficient (NTC) regime. This improvement is especially pronounced at the lowest temperatures we considered, which can be attributed to the important role of our calculated rate coefficients. At higher temperatures, both models underestimate fuel reactivity, and the prediction performances are comparable. In general, considering facility effects improves the performance of both models. The discrepancies between the experimental and modeling results at high temperatures may arise from other reactions that might control the high temperature combustion chemistry. The prediction performances of both models at pressures of 19 bar and 30 bar are similar to that at 9 bar (Figures S3 and S4 in supplementary material). For a better understanding of the roles of reactions R1-R7 in the ignition delay times, the individual effect of each reaction was analyzed and discussed in Figure S5 in supplementary material. Moreover, sensitivity analysis was carried out using the two models to highlight those reactions governing fuel auto-ignition process, which is presented in Figure S6 in supplementary material. The difference in sensitivity analysis results between both models suggests that the implementation of the calculated rate coefficients in the original model changes the fuel ignition chemistry.

The simulated concentration profiles of certain species in n-pentanol oxidation using both models are shown in Figures S7-S9, in supplementary material, along with the experimental data at a pressure of 10 atm, equivalence ratio of 1.0 and residence time of 0.7s [16]. The prediction results of two models are essentially same and in reasonable agreement with the experimental results. However, it is noted that both models slightly underestimate the overall formation of acetaldehyde (Figures S7-S9 (d)), 1-pentene (Figures S7-S9 (d)), hydrogen (Figures S7-S9 (c)) and methane (Figures S7-S9 (b)) at temperatures higher than 1000 K. Uncertainties in the rate coefficients ruling the yield of those species might be responsible for these discrepancies. For instance, as Heufer et al. [4] pointed out, the underestimation of 1-pentene might result from uncertainties in the rate coefficients of the β -scission reaction of 1-hydroxy-2-pentyl, as those rates were estimated from the analogous reaction in butanol. It is also important to highlight that when our calculated rate constants are implemented, the consumption of the fuel is in slightly better agreement with experiments.

The experimental and simulated laminar flame speed results of n-pentanol/air mixtures at atmospheric pressure and three different initial temperatures are plotted in Figure S10. At an initial

temperature of 353 K, both models predict the same results and reproduce the experimental results well; however, both models slightly underestimate the experimental predictions at higher initial temperatures of 433 K and 473 K. No distinct improvements are observed with the updated model, as expected based on the findings by Nativel et al. [8], whose sensitivity analysis pointed out that the laminar flame speed is more sensitive to the hydrogen-syngas-methane sub-mechanism rather than to the fuel-specific reaction system.

3.5 Role of the calculated rate coefficients in the yield of n-pentanal

In the kinetic model we used, several reactions contribute to the total yield of n-pentanal. One of them is the studied reaction R6, which competes with the reaction between 1-hydroxy-1-pentyl radical and oxygen ($R+O_2$) to directly form n-pentanal and HO_2 through a ro-vibrationally activated intermediate (well-skipping mechanism). The latter, which is barrierless, very exothermic, and very fast, would prevent the former from yielding n-pentanal, as no stabilized 1-hydroxy-1-peroxypentyl radical would be formed. However, at high pressures, when the 1-hydroxy-1-peroxypentyl intermediate radical can be stabilized, reaction R6 is expected to contribute to the n-pentanal yield. This competition is analyzed in Figure 10, where we plot the contribution of both reactions to the total amount of n-pentanal observed in the JSR simulations as function of temperature at 1 and 10 atm. We find that, as expected, reaction $R+O_2$ contributes the most to the formation of n-pentanal, especially at low temperatures when reaction R6 is not competitive due to its larger barrier height. Implementing our calculated rate coefficients for R6 into the original model reveals that this reaction is also able to contribute, to some extent, to the formation of n-pentanal, indicating its relevance to the understanding of the overall process. The prominence of reaction R6 is determined by pressure as well; at higher pressures, that is, 10 atm, when the intermediate radical 1-hydroxy-1-peroxypentyl is stabilized, reaction R6 plays an increasingly important role, and its n-pentanal yield increases with temperature and reaches a value of more than 9% at 1100 K, which can be observed in the inset plot in Figure 10.

For two larger $C_{10}H_{17}O_4$ α -hydroxy peroxy radicals derived from the atmospherically important monoterpene α -pinene, RRKM-ME modeling estimates that thermal stabilization of the activated

radical may be as large as 75-90 % and the concerted 1,4 H-shift and HO₂-loss (R6) is thus expected to be much more important [62]. We conclude that the larger the reaction system is, and the higher the pressure is, the more prominent is the concerted 1,4 H-shift and HO₂-loss, as the corresponding hydroxy-alkyl peroxy radical can be collisionally stabilized and can accommodate the excess energy more efficiently.

In the current study, the rate coefficients for the addition reaction $R+O_2 \rightarrow RO_2$ have not been computed, and those used by Heufer et al. [4], which come from the analogue reaction for the butyl radical determined experimentally by Lenhardt et al. [63], were used. This reaction might be decisive in the competition between reactions R6 and $R+O_2 \rightarrow n\text{-pentanal} + HO_2$ previously described; the calculation of its rate coefficients is beyond the scope of this work, and thus we carried out a brute force sensitivity analysis to examine its role in the outcome of that competition using the updated model. The results are presented in Figure S11 in the supplementary material, and we observe that reducing or increasing the rate constants for the association reaction $R+O_2 \rightarrow RO_2$ by a factor of 2 can reduce or increase, respectively, the yield of n-pentanal via reaction R6 by at most 10% at high temperatures and pressures. However, at low pressures and temperatures the uncertainties of $R+O_2 \rightarrow RO_2$ is only expected to play mild role in this matter. A similar analysis was performed for the competing reaction $R+O_2 \rightarrow n\text{-pentanal} + HO_2$, which is shown in Figure S12, and similar conclusions are obtained.

Despite the increasing prominence of reaction R6 as pressure and temperature are increased up to 10 atm and 1100 K, respectively, Figures S7-S9 indicate that both models predict similar n-pentanal yields at these conditions; this suggests that the increasing role of reaction R6 is not enough to make a difference in the n-pentanal yield. We expect that at higher pressures and temperatures, differences between the two models may arise, but to the best of our knowledge, experimental data at higher pressures and temperatures are not available.

4. Conclusions

In this work, seven intramolecular hydrogen-shift reactions of the 1-hydroxy-1-peroxypentyl radical, two of them involving a concerted HO₂ elimination, have been investigated theoretically. This

radical is an important species in the oxidation of n-pentanol. We performed CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ ab initio calculations and used the single structural variational transition state theory with small curvature tunneling corrections to obtain their barrier heights and approximated rate coefficients across a wide temperature range of 200-3000 K.

The concerted 1,4 hydrogen-shift and HO₂ elimination reaction yielding n-pentanal turned out to be the most prominent reaction of the 1-hydroxy-1-peroxypentyl radical consumption at all temperatures, as it has the lowest barrier height and the largest rate coefficients, making the other reactions unimportant. Therefore, this reaction was further investigated by refining its rate coefficients with the multistructural torsional variational transition state theory with small curvature tunneling corrections to account for the effect of the multiple conformers and torsional anharmonicity of reactant and saddle point species. This methodology was also used to investigate its reverse reaction, which shows a submerged barrier height with a negative temperature dependence and large rate coefficients at low temperatures, suggesting that this reaction might play a role in the atmospheric oxidation of n-pentanal. Due to the large number of conformers of the reactant species compared to that of the saddle point in both forward and reverse reactions, we observed that multistructural anharmonicity hinders reactivity and should be considered in the calculations. The rate coefficients calculated at 298.15 K are compared to those calculated using a previously presented cost-effective multi-conformer transition state theory approach, indicating the important role that multistructural anharmonicity plays in reactions involving species with numerous conformers.

Pressure dependent rate coefficients were also calculated using the system-specific quantum Rice-Ramsperger-Kassel theory, determining that at temperatures below 375 K, i.e. temperatures of interest in atmospheric chemistry, pressure does not play any role; however, at higher temperatures under combustion conditions, pressure effects are significant.

We used our calculated rate coefficients to update the kinetic model developed by Heufer et al. [4] for the oxidation of n-pentanol and checked its performance in predicting ignition delay times, species concentration profiles and laminar flame speeds at various conditions. While the original and the updated models predict essentially the same species concentration profiles and laminar flame speeds, the updated model yields some improvement in the ignition delay times at low and intermediate temperatures.

Our calculated rate coefficients also reveal the role of the concerted HO₂ elimination reaction in the production of n-pentanal. This reaction competes with the very fast, direct reaction between 1-hydroxy-1-pentyl radical and oxygen (R+O₂) forming n-pentanal and HO₂, through a rotationally activated intermediate. As pressure increases, the 1-hydroxy-1-peroxypentyl radical is stabilized and thus reaction R6 contributes more to the formation of n-pentanal.

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Scheme 1. Reactions that have been investigated in the present work.

Figure 1. Potential energy profiles in kcal/mol (electronic energy relative to the reactant (α -ROO)) at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level for reactions R1-R5 (a) and reactions R6 and R7 (b). The energies at the M06-2X/cc-pVTZ level are shown in parenthesis. Global minimum conformers of each species were used.

Figure 2. Transmission coefficients computed with the SCT method for reactions R1-R7

Figure 3. High pressure limit rate coefficients for reactions R1-R7 using the SS-VTST-HO-SCT method within the 200–500 K (a) and 500–3000 K (b) temperature ranges.

Figure 4. Multistructural anharmonicity factors (as defined by Eq. 8) for reactions R6 and -R6.

Figure 5. Plots of the high pressure limit rate coefficients of reactions R6 (a) and -R6 (b) with and without multistructural torsional anharmonicity (left y-axis) and their ratio (right y-axis).

Figure 6. Rate coefficients of the reaction $\alpha\text{-ROO} \rightarrow \text{aldehyde} \cdots \text{HO}_2$ for ethanol calculated by da Silva et al. [2] using the G3B3 method (left y-axis) and those for n-pentanol calculated in this study (left y-axis) along with their ratio (right y-axis).

Figure 7. Plots of pressure-dependent rate coefficients for R6.

Figure 8. Hydrogen abstraction and subsequent reactions that n-pentanol can undergo. Dominant pathways and species are shown with green and bolded arrows as well as with green boxes. For the unimolecular reactions of the peroxy radical in the green box, our calculated barrier heights (in kcal/mol) at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level are given.

Figure 9. Comparison of the predicted ignition delay times by the original [4] and updated models to the experimental data [6] at 9 bar

Figure 10. Yield of n-pentanal by the reactions R+O₂ and R6 in JSR simulations at 1 and 10 atm, equivalence ratio of 1.0 and residence time of 0.7 s. Reaction R6 was not implemented in the original model, so only the yield by reaction R+O₂ is shown for that model.