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Degradation of carbonyl hydroperoxides in the atmosphere and in combustion

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ABSTRACT: Oxygenates with carbonyl and hydroperoxy functional groups are important intermediates that are generated during the autooxidation of organic compounds in the atmosphere and during the autoignition of transport fuels. In the troposphere, the degradation of carbonyl hydroperoxides leads to low-vapor-pressure polyfunctional species that may precipitate in clouds and fog droplets or to the formation of secondary organic aerosols (SOAs). In combustion, the fate of carbonyl hydroperoxides is important for the performance of advanced combustion engines, especially for autoignition. A key fate of the carbonyl hydroperoxides is reaction with OH radicals, for which kinetics data are experimentally unavailable. Here, we study 4-hydroperoxy-2-pentanone ($\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}(\text{OOH})\text{CH}_3$) as a model compound to clarify the kinetics of OH reactions with carbonyl hydroperoxides, in particular H-atom abstraction and OH addition reactions. With a combination of electronic structure calculations, we determine previously missing thermochemical data, and with multipath variational transition state theory (MP-VTST), a multidimensional tunneling (MT) approximation, multiple-structure anharmonicity, and torsional potential anharmonicity we obtained much more accurate rate constants than the ones that can be computed by conventional single-structure harmonic transition state theory (TST) and than the empirically estimated rate constants that are currently used in atmospheric and combustion modeling. The roles of various factors in determining the rates are elucidated. The pressure-dependent rate constants for the addition reaction are computed using system-specific quantum RRK theory. The calculated temperature range is 298–2400 K, and the pressure range is 0.01–100 atm. The accurate thermodynamic and kinetics data determined in this work are indispensable in the global modeling of SOAs in atmospheric science and in the detailed understanding and prediction of ignition properties of hydrocarbons and alternative fuels.

1. INTRODUCTION

Biologically generated and anthropogenic organic compounds are precursors for tropospheric ozone and secondary organic aerosols (SOAs).¹ The atmospheric autooxidation of organic compounds is usually initiated from reactions with oxidants, e.g., OH, NO₃, and O₃, to produce radical intermediates, which then react with O₂ and form peroxy radicals (RO₂). The fates of peroxy radicals play important roles in the degradation of organic compounds, which undergo intramolecular H-atom migration or bimolecular reactions with HO₂, NO, RO₂, etc.^{2,3}

Oxygenates with carbonyl and hydroperoxy functionalities constitute an important class of intermediates in organic autooxidation. Recent studies have shown that the ozonolysis of unsaturated organic compounds (e.g., long-chain alkenes and monoterpenes) leads to highly oxidized molecules with multiple carbonyl and hydroperoxy functional groups, and these are a major source of SOAs.^{4,5}

Scheme 1a–c shows the potential reaction pathways to carbonyl hydroperoxides from the atmospheric autooxidation of alcohols, ketones, and peroxides. The reactions of carbonyl hydroperoxides with OH radicals are expected to be important degradation routes in the troposphere.^{2,5} The resulting carbonyl hydroperoxy radicals may react with O₂ and lead to large RO₂ radicals. The further reactions of the large RO₂ radicals lead to low-vapor-pressure intermediates, which may precipitate in cloud and fog droplets or in the formation of SOAs. The reaction with OH is also important in combustion, where OH radicals are known to be important in all stages of ignition.⁶

The chemistry of peroxy radicals also controls the autooxidation of organic compounds in combustion (e.g., at 500–700 K).⁷ The intramolecular H-atom migration of peroxy radical, followed by O₂ addition, intramolecular H-atom migration, and decomposition produces carbonyl hydroperoxides.^{8–10} Scheme 1 shows the pathway to a car-

bonyl hydroperoxide from the autooxidation of *n*-pentane and other compounds. The produced carbonyl hydroperoxide serves as a major chain-branching agent in hydrocarbon autoignition.^{7,11-15} On one hand, carbonyl hydroperoxides (HOOQ'=O) allow low-temperature chain branching because they have hydroperoxy groups with weak O–O bonds that decompose easily to OH and alkoxy radicals. On the other hand, the H-atom abstraction reactions on carbonyl hydroperoxides may play a significant role, thus decreasing the chain branching effect of the competing initiation reactions. Therefore we must know the fate of carbonyl hydroperoxides to engage in accurate ignition modeling. However, the H-abstraction from carbonyl hydroperoxides is seldom considered in kinetics modeling,¹⁶ and the reaction pathways and kinetics are not well known.¹⁷⁻¹⁹ Furthermore, it is almost impossible to measure the rates of these H-abstraction reactions because carbonyl hydroperoxide species are very reactive; therefore theoretical calculations can fill a gap in the knowledge that is essential for understanding carbonyl hydroperoxide chemistry.

Scheme 1. Reaction scheme for the production of carbonyl hydroperoxide from the autooxidation of (a) 2-pentanol, (b) 2-pentanone, (c) 2-pentylperoxide, and (d) *n*-pentane.

In this work, we select a pentyl carbonyl hydroperoxide (4-hydroperoxy-2-pentanone) as a model compound to investigate the kinetics of the reaction of OH with a carbonyl hydroperoxide; 4-hydroperoxy-2-pentanone is a keto hydroperoxides, and it will be called KHP for convenience hereafter. The reaction mechanism including both H-atom abstraction and OH radical addition is presented in Scheme 2. As described in previous studies by Sharma et al.²⁰ and Goldsmith et al.,²¹ hindered internal rotation in hydroperoxy and alkylperoxy radicals cannot be described accurately by independent 1D rotors due to variations in the torsional barriers that arise from the presence or absence of hydrogen bonding interactions. These fascinating features prompt us to explore the kinetics of H-abstraction of carbonyl hydroperoxide to elucidate the species responsible for chain branching reactions, as well as for SOA formation.

In this work, we compute the potential energy surfaces for hydrogen abstraction from different sites of KHP by OH radical and then use multi-path variational transition state theory^{22,23} (MP-VTST) with multi-dimensional tunneling contributions²⁴ to compute the rate constants for producing each of the possible products. These rate calcu-

lations include multiple-structure anharmonicity and torsional potential anharmonicity. We also consider the addition reaction, for which we use system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) theory with the Lindemann-Hinshelwood thermal activation mechanism²⁵⁻²⁷ to compute the thermal rate constants as functions of pressure.

2. METHODS

2.1 Electronic structure methods. As the first step, an exhaustive conformational search was carried out by optimizing all the initial conformers that are generated through rotating all the torsional bonds (except for methyl group) using the *MSTor* program.²⁸⁻³⁰ The preliminary conformational structure search and geometry optimization were performed using the Mo8-HX exchange correlation functional³¹ with the MG3S basis set. The MG3S basis set³² is identical to the 6-311+G(2df,2p) basis set^{33,34} for H, C, and O atoms.

Scheme 2. Reactions of OH with 4-hydroperoxy-2-pentanone. (R1-R5): hydrogen abstraction; (R6): the formation of the stabilized intermediate adduct; (R7): hydroxide addition followed by decomposition of an intermediate to form bimolecular products. Products are labeled with the prefix P; and transition states are labeled with the prefix TS.

Single-point energy calculations were performed at Mo8-HX/MG3S geometries using eleven density functionals^{31,35-44} with the MG3S and jul-cc-pVTZ⁴⁵ basis sets. To test and validate the density functionals for the present dynamics calculations, we performed benchmark calculations by the explicitly correlated electronic structure

method CCSD(T)-F12a^{46,47} with the jun-cc-pVTZ basis set.⁴⁸ The CCSD(T)-F12a/jun-cc-pVTZ calculations can be viewed as an efficient way to approximate the complete basis set (CBS) limit of the CCSD(T) method.⁴⁹

The distinguishable conformers that were found by the preliminary conformer search with the Mo8-HX/MG3S method were re-optimized by the electronic structure method selected on the basis of having the smallest MUE in the tests of the previous paragraph. Frequency analyses were also performed by that method.

Both the SCF calculations and the geometry optimizations were performed with tight convergence criteria. The density functional integrations were carried out by a grid of 99 radial shells per atom with 974 angular points per shell. All the electronic structure calculations were performed using *Gaussian 09* software⁵⁰ with the locally developed *MN-GFM6.7* module.⁵¹ The CCSD(T)-F12a calculations were carried out by using the *Molpro* program.⁵²

2.2 Thermodynamics and Kinetics. The multistructural method with coupled torsional-potential anharmonicity⁵³ (MS-T) was used for calculating enthalpies, entropies, and heat capacities as functions of temperature. The MS-T partition functions were calculated using the *MSTor* code.²⁸⁻³⁰ All structures have a rotational symmetry number of 1.

We carried out first-principles direct dynamics calculations using multistructural canonical variational transition state theory with small curvature tunneling (MS-CVT/SCT)⁵⁴ to calculate the high-pressure-limit rate constants of reactions R1-R6. For the hydrogen abstraction reactions R1-R5 we also performed calculations by more complete multipath canonical variational transition state theory with small curvature tunneling (MP-CVT/SCT).^{22-24,53,55,56} And for the current system which contains one chiral carbon, we follow the procedures in the previous paper⁵⁶ for treating chiral centers in MS- and MP-VTST theory. The dynamics calculations were performed using the *Polyrate 2016-2A*⁵⁷ and *Gaussrate 2017* codes.⁵⁸

The minimum energy paths (MEPs) needed for the calculations were calculated in isoinertial coordinates using the Page-McIver method, which is called the local quadratic approximation (LQA) in the original reference,⁵⁹ and using the reorientation of the dividing surface (RODS) algorithm.⁶⁰ The step size was 0.0026 Å, and the Hessians were updated every 10 steps along the reaction path. Vibrational frequencies were scaled by 0.975, as determined in a standard way,⁶¹ to account for vibrational anharmonicity and systematic errors in the electronic structure.

Vibrational frequencies along the reaction path were calculated using nonredundant internal coordinates^{62,63} for R2-R6. For R1, redundant internal coordinates⁶⁴ were used because it has a doubly degenerate linear bend.⁶⁵

The multidimensional tunneling contributions (MT) for each path were evaluated with the small-curvature tunneling approximation (SCT).^{24,66} The vibrationally adiabatic ground-state energy, which is the effective potential for tunneling, is given by:

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

where s is the reaction coordinate, which is a signed distance from the saddle point along each curved MEP in

isoinertial coordinates, $V_{\text{MEP}}(s)$ is the potential energy along the MEP, and $\varepsilon^G(s)$ is the local zero point energy.

The MS-VTST rate constants are calculated by⁵⁴

$$k^{\text{MS-CVT/SCT}} = F_{\text{act}}^{\text{MS-T}} k_1^{\text{SS-CVT/SCT}} \quad (2a)$$

where $k_1^{\text{SS-CVT/SCT}}$ is the single-structural canonical variation theory⁶⁷ (CVT) rate constant with the multidimensional small curvature tunneling (SCT) approximation,²⁴ which employs the lowest-energy structure (labeled as 1 here) for reactants and the transition state. $F_{\text{act}}^{\text{MS-T}}$ is the multi-structural torsional anharmonicity factor of the reaction – it includes the contributions from all the conformational structures of the reactants and the transition state and is computed by the coupled-potential MS-T method as described elsewhere.^{25-27,55} It is computed by

$$F_{\text{act}}^{\text{MS-T}} = F_{\text{TS}}^{\text{MS-T}} / F_{\text{R}}^{\text{MS-T}} \quad (2b)$$

where $F_{\text{X}}^{\text{MS-T}}$ is the multistructural torsional anharmonicity factor of species X, and it equals the ratio of the MS-T partition function to the single-structure harmonic one. As in the original MS-VTST method, $F_{\text{TS}}^{\text{MS-T}}$ was approximated by its value at the conventional transition state. In the MS-T method, the potential for the torsional coordinate $\phi_{j,\tau}$ of torsion τ of structure j of a given species is approximated locally as

$$V_{j,\tau} = U_j + A_{j,\tau} [1 - \cos M_{j,\tau}(\phi_{j,\tau} - \phi_{j,\tau,\text{eq}})] \quad (2c)$$

where U_j is the energy of the structure, $\phi_{j,\tau,\text{eq}}$ is the equilibrium value of the torsion angle, $M_{j,\tau}$ is the local periodicity, determined by Voronoi tessellation, and $A_{j,\tau}$ is determined from the second-order force constants and the local periodicities.⁵³ Effects caused by the deviation of eq 2c from a harmonic potential are called torsional potential anharmonicity effects; the effect of including the contributions of all the distinguishable structures of a species (a reactant species or a transition state) is called multiple-structure anharmonicity. The combination of these two effects is called multistructural anharmonicity.

MP-VTST is an extension of multi-structural variational transition state theory, and the MP-VTST rate constants are

$$k^{\text{MP-CVT/SCT}} = F_{\text{act}}^{\text{MS-T}} \langle \gamma \rangle_P k_1^{\text{ConTST}} \quad (2d)$$

Here k_1^{ConTST} is the conventional transition state theory rate constant calculated by using the global minimum reactant and global-minimum transition structure without tunneling (calculations with quantized vibrational levels but without tunneling are called quasiclassical); and $\langle \gamma \rangle_P$ is the path-averaged generalized transmission coefficient,⁶⁸ which includes, for each reaction path, both the variational effect and the multidimensional tunneling (MT) contributions:

$$\langle \gamma \rangle_P = \frac{\sum_{p=1}^P \kappa_p^{\text{MT}} \Gamma_p^{\text{CVT}} Q_p^{\text{SS-T}}}{\sum_{p=1}^P Q_p^{\text{SS-T}}} \quad (3)$$

where P is the number of reaction paths involved in the MP-VTST calculations, and $Q_p^{\text{SS-T}}$ is the single-structural rovibrational partition function of the transition state computed with torsional anharmonicity for path p ; Γ_p^{CVT} is the recrossing transmission coefficient for path p ; and κ_p^{MT} is the multidimensional tunneling transmission coefficient for path p .

Note that the recrossing transmission coefficient could also be called the quasiclassical transmission coefficient; it is also sometimes called the variational effect because it accounts for the difference between variational transition state theory and conventional transition state theory when both are applied without tunneling. Its deviation from unity is a measure of the extent to which VTST accounts for the breakdown of the no-recrossing assumption of quasiclassical transition state theory at the conventional transition state that passes through the saddle point. (For example, a recrossing transmission coefficient of 0.7 means that 30% of the quasiclassical flux through the conventional transition state does not contribute to the net one-way flux because the true dynamical bottleneck is the variational transition state, not the conventional transition state.)

Reactions R6 and R7 (see Scheme 2) have pressure-dependent rate constants because there is a unimolecular intermediate (P6) in the reaction mechanism. These reactions can be described by the following chemical activation mechanism:²⁵

where T is temperature, M is the bath gas, P6^* is the energized adduct, P6 is the (stabilized) addition product, k_c is the collisional deactivation rate constant, and $k_{\text{conv}}(E)$ is the energy-dependent unimolecular dissociation rate constant of the energized species P6^* , i.e., the rate constant for conversion of the energized intermediate to product.

The formation of the stabilized adduct P6 is called reaction R6 and the rate constant for producing stabilized P6 is denoted as k_{R6} and is defined as $(d[\text{P6}]/dt)/([\text{OH}][\text{KHP}])$. The unimolecular dissociation of P6^* to produce P7 and CH_3COOH is defined as reaction R7; and the rate constant for the formation of P7 and CH_3COOH is defined as $k_{\text{R7}} = d[\text{P7}]/dt)/([\text{OH}][\text{KHP}])$. The pressure-dependent rate constants k_{R6} and k_{R7} were computed using system-specific quantum RRK theory^{25,26} (SS-QRRK) combined with the chemical activation mechanism. The critical energy and frequency factor of the SS-QRRK treatment are set equal to the high-pressure-limit temperature-dependent Arrhenius parameters (see SI for the activation energy for each reaction) computed from the fitting formula (see eqs 4 and 5 in section 3.5) for the rate constants. The L-J potential parameters needed for k_c were chosen as follows: $\sigma_1 = 5.71 \text{ \AA}$, $\epsilon_1/k_B = 510.67 \text{ K}$ for P6 ; and for the bath gas Ar, $\sigma_2 = 3.47 \text{ \AA}$ and $\epsilon_2/k_B = 114.0 \text{ K}$ respectively. The average energy transferred per deactivating collision, which plays an important role in the falloff effect,⁶⁹ is taken to be $\langle \Delta E \rangle_{\text{down}} = \Theta(T/300)^{0.85}$ with $\Theta = 300 \text{ cm}^{-1}$; this simple power law representation for $\langle \Delta E \rangle_{\text{down}}$ has proven to allow for a reasonable reproduction of experimental data across a wide range of temperature and pressure.⁷⁰⁻⁷² In previous work, Jalan et al.⁷³ adopted a value of 150 cm^{-1} for Θ for the ketohydroperoxide of pro-

pane; based on this and the empirical rule that “larger species generally having larger values”,⁷⁰⁻⁷² the value of Θ is taken as 300 cm^{-1} in the present paper (and we will also report sensitivity checks). The formulas relating k_c to $\langle \Delta E \rangle_{\text{down}}$ are given elsewhere.^{26,74}

3. RESULTS AND DISCUSSION

3.1 Electronic structure calculations. In this work, we tested eleven density functionals. Comparing with the relatively accurate CCSD(T)-F12a/jun-cc-pVTZ method, the Mo8-HX/jul-cc-pVTZ method was selected as an affordable electronic structure method because it has the smallest mean unsigned error (MUE), in particular 0.51 kcal/mol for the forward and reverse barrier heights and energies of reaction (21 data points). Full details of these tests are given in the Supporting Information (SI). Table 1 shows the calculated forward barrier heights using our selected method and the benchmark.

Table 1. Calculated forward barrier heights (kcal/mol) for R1-R6.

	Forward barrier height					
	R1	R2	R3	R4	R5	R6
Mo8-HX	-0.08	-4.76	-2.73	1.06	1.15	0.79
CCSD(T)	0.99	-4.38	-2.61	0.88	1.44	2.60

3.2 Multistructural torsional anharmonicity. All of the torsional bonds except the methyl group were rotated by 0, 120, and -120 degrees to generate various initial conformational structures. The torsional potential anharmonicity of all the torsions, including the methyl groups (which do not generate additional distinguishable structures) are included in the partition functions; and in this work, the MS-T partition functions are computed at a full⁷⁵ high-level (i.e., by Mo8-HX/jul-cc-pVTZ). For KHP and TS1-TS6, the numbers of torsions (excluding the CH_3 group) and distinguishable structures for KHP and TS1-TS6 are 4/38, 7/179, 6/50, 6/90, 6/59, 7/136 and 5/74 respectively.

The numbers of distinguishable structures in each of nine energy ranges for each of the species are shown in Figure 1. For KHP, the energy difference between the lowest and highest of the 38 structures is relatively small, being equal to 6.2 kcal/mol. However for TS1, the energy difference between the lowest and highest of the 179 structures is relative largely, being 9.9 kcal/mol.

Figure 1. Number of distinguishable conformers in each relative potential energy range for reactant (KHP), and transition states (TS1–TS6). For KHP, the energy of the global-minimal structure is chosen as the zero of the relative energy, and for the transition states the energies are relative to the lowest-energy transition state for that reaction.

Table 2 illustrates the effect of multiple-structure anharmonicity and torsional potential anharmonicity on the partition functions of KHP by comparing the conformational-rotational-vibrational partition function of KHP calculated by using the multistructural approximation with torsional anharmonicity (MS-T) and the multistructural local harmonic (MS-LH) approximation to the rotational-vibrational partition function of the lowest-energy structure (which is the single-structure harmonic (SS-HO) approximation). The MS-LH approximation, which neglects torsional potential anharmonicity but includes multiple-structure anharmonicity, overestimates the best estimate by 4–22% at 298–1000 K, but by much greater amounts (up to a factor of 2.3) at higher temperatures. The MS-T approximation exceeds the SS-HO result by a factor increasing from 13 at 298 K to 162 at 2400 K. Therefore, the standard approach found in textbooks that ignores multiple structures introduces large errors in partition functions.

All the local periodicities of structures of the reactant and of transition states TS2 and TS3 are given for illustration in Figure 2. (The local periodicities of TS1 and TS4–TS6 are provided in the SI.) The physical meaning of the $M_{j,\tau}$ parameter was explained in detail in the original MS-T paper,⁷⁶ but a rough explanation is that it tells us the average effective numbers of minima along the torsional coordinates. Figure 2 shows that the local periodicities are usually between 2 and 3. The most significant reason why we see a variety of $M_{j,\tau}$ values in Figure 2 is the influence of hydrogen bonding in some of the structures.

Table 2. Conformational-rotational-vibrational partition functions of KHP with the multi-structural torsional method (MS-T) and multistructural local harmonic (MS-LH) approximation including all structures and the single-structure harmonic rotational-vibrational partition function (SS-HO) of the lowest-energy structure of KHP.^a

$T(K)$	$Q_{\text{con-rovib}}^{\text{MS-T}}$	$Q_{\text{con-rovib}}^{\text{MS-LH}}$	$Q_{\text{rovib},1}^{\text{SS-HO}}$
298	5.84E-59	7.15E-59	4.64E-60
400	3.43E-40	3.81E-40	1.27E-41
600	9.36E-21	9.76E-21	1.41E-22
800	4.98E-10	5.33E-10	4.68E-12
1000	6.81E-03	7.78E-03	4.93E-05
1500	1.12E+09	1.61E+09	6.36E+06
2400	2.38E+20	5.44E+20	1.47E+18

^aThe zero of energy for the partition functions is the energy of the lowest-energy classical equilibrium structure.

Figure 2. The unitless local periodicities $M_{j,\tau}$ for KHP, TS2, and TS3.

A hydrogen bond lowers the barrier by stabilizing the transition state. However the entropic effect of hydrogen bonding can increase the free energy of activation.⁵⁶ We analyzed the hydrogen bonding by adopting the criteria defined by Chen et al.⁷⁷ by which a normal hydrogen bond has the H...O distance less than 2.4 Å and the O-H...O angle greater than 150°, whereas we identify a “strongly bent hydrogen bond” as one with an H...O distance less than 2.4 Å and the O-H...O angle in the range 90–150°. Figure 3(a) shows some TS structures for reactions R2 and R3; the first P paths for each reaction are ordered by increasing values of their classical barrier heights and are denoted as path 1, path 2, and so on. There are two strongly bent hydrogen bonds for most of the TS2 conformers. Also TS3(path 1) has a strongly bent hydrogen bond, and TS3(path 2) has a normal hydrogen bond.

Figure 3(b) shows the relative enthalpies and free energies of transition structures for R3, both with and without a hydrogen bond. The figure shows that a non-hydrogen-

bonded transition structure, e.g. conformer 10, although it has a higher enthalpy of activation, does not necessarily have a higher free energy of activation than conformers with hydrogen bonds (conformers 1–8) at 800 K and 2000 K. This is due to the hydrogen bond reducing the entropy. Therefore a non-hydrogen-bonded structure can contribute more to the rate constant than some hydrogen-bonded conformer. This phenomenon was also found in a previous study.⁵⁶

Figure 3. (a) Hydrogen bonding analysis for TS2 (path 1 and path 2) and TS3 (path 1 and path 2), where TS2 and TS3 are the transition state structures of R2 and R3 respectively. (b) Relative enthalpy of activation (H) and relative Gibbs free energy of activation (G) (both in kcal/mol) for TS3 (paths 1 to 20). The conformers are arranged in order of increasing classical barrier height. Paths 1–8 have hydrogen bonds; paths 9–20 do not have hydrogen bonds. In this figure, the thermodynamic quantities are anharmonic results for the individual structures, as calculated by MS-T, and the zero of energy is set equal to the potential energy of the energetically lowest conformer of the transition state structure that corresponds to path 1.

Classical barrier heights ($V^\ddagger$) and quantum mechanical quasithermodynamic quantities for these examples of hydrogen-bonded transition states are in Table 3. The energy barriers relative to KHP + OH are negative, showing some stabilization; however, this does not necessarily indicate fast reaction because the entropy effect should

also be taken into account. The path with the highest barrier, namely TS3(path 2), has a larger entropy than others, this reduces the free energy of activation. In fact, it has the most favorable free energy of the four cases shown, even though it has the least favorable barrier. This shows that the effects of hydrogen bonding are subtle.

Table 3. Classical barrier heights (kcal/mol) and standard-state entropies (cal/K/mol), and free energies (kcal/mol) of selected conventional transition states (saddle points).^a

$T(K)$	S°	G°	S°	G°
	TS2(path 1)		TS2(path 2)	
	$V^\ddagger = -4.8$		$V^\ddagger = -3.5$	
298	104.0	68.6	106.1	69.3
400	118.0	57.3	120.1	57.7
600	142.4	31.2	144.5	31.2
800	163.3	0.6	165.4	0.1
1000	181.5	-34.0	183.6	-34.8
1500	218.2	-134.3	220.3	-136.2
2400	265.4	-353.3	267.5	-357.1
	TS3(path 1)		TS3(path 2)	
	$V^\ddagger = -2.7$		$V^\ddagger = -2.4$	
298	105.9	69.3	106.9	69.3
400	120.0	57.8	120.8	57.7
600	144.4	31.3	145.0	31.1
800	165.3	0.3	165.9	-0.1
1000	183.3	-34.6	184.1	-35.1
1500	220.0	-135.9	221.2	-136.9
2400	267.1	-356.5	268.6	-358.7

^aThe zero of energy is KHP + OH. The standard state pressure is a 1 bar ideal gas.

Figure 4 shows the multistructural torsional anharmonicity factor F_X^{MS-T} for each species and F_{act}^{MS-T} for each reaction at 298–2400 K. It shows that F_X^{MS-T} is in the range 12–161, 8–2077, 3–219, 5–562, 16–296, 9–951, and 3–1782 for X = KHP and TS1–6, respectively. The multistructural torsional anharmonicity is especially large for TS1 and TS6 for $T > 600$ K. The multistructural anharmonicity factors for the reactions are smaller than the corresponding transition state factors due to cancellation with F_X^{MS-T} of the reactant KHP. The multistructural torsional anharmonicity factors F_{act}^{MS-T} are spread over the ranges 0.6–13, 0.2–1.4, 0.4–3.5, 1.3–1.8, 0.7–5.9, and 0.2–11 for R1–R6, respectively. Because these ranges are quite different for the different reactions, multistructural anharmonicity has a large effect on the branching ratios.

Figure 4. Multistructural torsional anharmonicity factor (a) for species, KHP and TS1-TS6; (b) for every forward reactions (R1-R6).

Because we have seen that multistructural anharmonicity plays a significant role in the partition functions, we know that it affects the accuracy of the thermodynamic quantities, such as standard-state entropy, heat capacity, relative enthalpy, and relative Gibbs free energy. Table 4 lists these quantities for KHP at 298–1000 K; results at higher temperatures are in the SI. The entropy and heat capacity obtained by the popular group additivity (GA) method^{78,79} are given for comparison. The heat capacities calculated with the MS-T method considering both multistructural and torsional anharmonicity deviate by ~ 3 cal mol⁻¹ K⁻¹ from those obtained by the GA method at most temperatures. The MS-LH method overestimates the heat capacities especially at high temperatures (≥ 700 K). In the temperature range of 298–600 K, the entropies calculated with MS-T and MS-LH are almost identical and are in reasonable agreement with those obtained by the GA method. As the temperature increases, the entropies estimated by the widely used GA method show large deviations ($3\text{--}10$ cal⁻¹ mol⁻¹ K) from our calculated values by the MS-T method. The SS-HO approximation has poor accuracy at all temperatures, e.g., at 298 K, it differs by up to 9 cal⁻¹ mol⁻¹ K from the MS-T result. Due to the increasing contribution of multistructural anharmonicity with increasing temperature, the entropies calculated with MS-T and MS-LH have dramatically large deviations from those

calculated by the SS-HO method and from the empirical GA results.

3.3 Variational effects. For each reaction, we included the four lowest-energy reaction paths in the MP-VTST calculations (i.e., $P = 4$). As mentioned above, the first four paths are ordered by increasing values of their classical barrier heights and are denoted as path 1, path 2, The potential energy along the minimum energy path (V_{MEP}) and the vibrationally adiabatic ground-state potential energy (V_a^G) for R2 (paths 1–4) are displayed in Figure 5. Note that a vibrationally adiabatic potential-energy curve is the same as a free energy of activation profile for $T = 0$ K; for all four paths of reaction R2, the location of the canonical variational transition state is near -0.185 Å at 0 K. At finite temperatures, the free energy of activation profiles differ from the V_a^G curve, and the location of variational transition state is determined by the maximum of the free energy of activation profile. For instance, for path 1, at 298 K, 600 K, 1000 K, 1500 K and 2400 K, the variational transition state is at -0.180 , -0.182 , -0.189 , -0.201 , and -0.224 Å, respectively, and the vibrationally adiabatic potential energy at these locations are all in the range 93.03–93.06 kcal/mol. For path 2, the location of the variational transition state at these temperatures is -0.179 , -0.195 , -0.221 , -0.254 , and -0.310 Å, and the corresponding vibrationally adiabatic ground-state energies are correspondingly 94.28, 94.28, 94.25, 94.19, and 94.06 kcal/mol. For path 1 to path 4, as the classical barrier height increases, V_{MEP} and V_a^G barriers become thinner, which is reflected in the tunneling transmission coefficients discussed in section 3.4.

Figure 6 shows the CVT recrossing transmission coefficients for the four lowest-energy paths of R2. The results for the different paths agree with each other within a factor of 1.6, and the variational effect is significant, especially at low temperatures, e.g., the conventional TST rate constant is a factor of 8 larger than the CVT one at $T = 300$ K for R2.

The recrossing transmission coefficients of reactions R1–R6 are shown in Figure 7. For R2, R3, R4, and R5, the recrossing transmission coefficients are between 0.1 to 0.6 over the whole temperature range. What causes these large variational effects? To answer this we analyzed the vibrational frequencies along the reaction path. The results for R2 are shown in Figure 8, and the vibrational frequencies for some other reactions are provided in the SI. We find that the variational effect is mainly due to the one vibrational mode that changes dramatically along the reaction path. This mode (ν_{in} , shown as a dashed curve in Figure 8) is the H–C stretch of the breaking bond in the reactant region, then it decreases by ~ 1000 cm⁻¹ from reactants to the saddle point, where is a quasisymmetric C–H–O stretching mode, and finally it increases as it transforms into the vibration of the new H–O bond in the product. The reason for the decrease in the middle region is that the mode has less hydrogenic motion in that region where the hydrogenic motion is mainly in the reaction coordinate, which is an asymmetric C–H–O stretching motion there. The decrease in the middle region of

the reaction path significantly increases the vibrational partition function of the generalized transition state when it is calculated relative to the local potential energy minimum. While the vibrational frequency is changing rapidly, the potential energy change from $s = 0$ to $s = -0.106$ Å is less than 1.1 kcal/mol, which can be seen from the relatively flat potential energy surface around the saddle point in Figure 5, so the vibrational partition function relative to V_{MEP} changes more than the Boltzmann factor of V_{MEP} . Therefore it is necessary to use variational transition state theory (rather than conventional transition state theory) for treating such a reaction. This kind of large variational effect due to the mode that transforms from the bond-breaking vibration to the bond-forming vibration has been observed for many reactions in previous studies.^{64,65,67,68,80-86}

We have discussed the effect of the key high-frequency modes, which are most important at low T . As the temperature increases, the lower frequencies can be very important. The lower frequencies are shown in the SI.

Figure 5. Vibrationally adiabatic ground-state potential energy curve (V_a^G) and the potential energy (V_{MEP}) along the minimum energy path for paths 1, 2, 3, and 4 of R2. Here s is the signed distance from the saddle point along each curved MEP in isoinertial coordinates scaled to a reduced mass of 1 amu.

Figure 6. Canonical recrossing transmission coefficients (Γ^{CVT}) for R2 at various temperatures. Γ^{CVT} are defined as the ratios of rate constants computed by quasiclassical variational TST to those computed by quasiclassical conventional TST.

Figure 7. Canonical recrossing transmission coefficients (Γ^{CVT}) for R1-R6 at various temperatures.

Figure 8. The eleven highest vibrational frequencies of R2 as functions of the reaction coordinate s . The saddle point is at $s = 0$.

3.4 Multidimensional tunneling effect. The multidimensional tunneling transmission coefficient includes the quantum mechanical tunneling effect and the contribution from nonclassical reflection at energies above the effective barrier. In the present work, using the vibrationally adiabatic ground-state potential energy as the effective potential curve and including corner-cutting tunneling by means of the effective mass, the small-curvature tunneling (SCT) approximation is used to calculate the multidimensional tunneling transmission coefficients. The multidimensional SCT tunneling transmission coefficients for the lowest-energy reaction paths (path 1 for each reaction) are plotted as functions of temperature in Figure 9 for R1-R6. These tunneling transmission coefficients show essentially no tunneling for R2 and R3 and range from 1.3 to 3.5 at 298 K for the other four reactions. The tunneling transmission coefficient for R5 is the largest among the lowest-energy paths for these six reactions, and it is 1.5 even at 600 K.

Figure 10 shows the calculated tunneling transmission coefficients of R2 for paths 1, 2, 3, and 4. They are consistent with the previously discussed V_a^G curves. As expected, the path with the highest energy barrier has the largest tunneling transmission coefficient. Comparing path 1 with path 4, we see a factor of 2.4 difference at room temperature.

Figure 9. Small-curvature tunneling transmission coefficients κ^{SCT} (for path 1) of reactions R1-R6 at 298-2400 K.

Figure 10. Small-curvature tunneling transmission coefficients κ^{SCT} of R2 for path 1 through path 4 at 298-1000 K.

3.5 MP-CVT/SCT rate constant. Path-averaged generalized transmission coefficients of reactions R1-R5 are in Table 5 for $P = 1, 2$, and 4 in eq 3. These coefficients include the path-dependent variational effect and the path-dependent multidimensional tunneling effect. For example, for R2, the multidimensional tunneling coefficient from path 1 to path 4 increases (as shown in Figure 10), but the recrossing transmission coefficient is a nonmonotonic function of path label (as shown in Figure 6). Also, the single-structural rovibrational partition functions of the transition state computed with torsional anharmonicity are nonmonotonic functions of path number. These three factors all contribute to the final $\langle \gamma \rangle_P$. The resulting differences of $\langle \gamma \rangle_2$ from $\langle \gamma \rangle_4$ are 12% or less for R2-R5, but as large as 42% for R1. This shows that thermal rate constants can be significantly impacted by the higher-energy paths.

Since the forward reactions studied here are exoergic, we adopted the following fitting equations^{23,69} for the rate constants in the temperature range between 298 and 2400 K:

$$k = A \left(\frac{T+T_0}{300} \right)^n \exp \left[-\frac{E(T+T_0)}{R(T^2+T_0^2)} \right] \quad (4)$$

where A , n , E , T_0 are fitting parameters, and the ideal gas constant R is $0.00198 \text{ kcal mol}^{-1} \text{ K}^{-1}$. The fitting parameters are tabulated in the SI.

The temperature-dependent Arrhenius activation energies E_a can be derived from the local slopes of Arrhenius plots. For exothermic reaction, the resulting formula is:

$$E_a = \frac{E(T^4+2T_0T^3-T_0^2T^2)}{(T^2+T_0^2)^2} + \frac{nRT^2}{T+T_0} \quad (5)$$

The temperature-dependent Arrhenius activation energies for R1-R6 are plotted in Figure 11. The activation energy increases dramatically with increasing temperature, especially in the temperature range of 298-600 K. For instance, the deviation between 298 K and 600 K is 3.2, 12.8, 4.4, 0.8, 3.3 kcal/mol in the MP-CVT/SCT calculations for R1-R5 respectively. The MS-CVT/SCT activation energies are close to the MP-CVT/SCT ones except for R2, where the difference is due to the path dependence of quantum mechanical tunneling and multistructural anharmonicity.

Figure 11. High-pressure-limit activation energies for R1-R6 at 298-2400 K. These symbols represent the MS-CVT/SCT results, and the lines are the MP-CVT/SCT results.

Figure 12. Calculated high-pressure-limit rate constants for R1-R6 at 298-2400 K using MP-CVT/SCT and MS-CVT/SCT. These symbols represent the MS-CVT/SCT results, and the lines are the MP-CVT/SCT results. We also compare to previous data for R2 which are from previous empirical model studies by Ranzi et al.¹⁶ and Bugler et al.¹⁹

Figure 12 shows the final high-pressure-limit MP-CVT/SCT rate constants and the MS-CVT/SCT ones for R1-R6 in the temperature range of 298-2400 K. There are four noteworthy aspects: (i) For R1, R2, R3 and R5, the final MP-CVT/SCT rate constants and the MS-CVT/SCT ones are almost identical. (ii) The H-abstraction reactions (R1-R5) have larger rate constants than the addition reaction (R6). (iii) R2 and R3 have a stronger negative temperature dependence effect than the other reactions. (iv) At low temperatures (298-400 K), the rate constants of R2 and R3 are close to each other, and R3 begins to dominate as temperature is raised. We can explain aspect iv by a combination of three factors: (1) the entropy of R3 is ~ 2 cal/mol/K larger than R2 (as can be seen in Table 3); (2) the influence of $T\Delta S$ is larger than the reaction enthalpy, especially at higher temperatures; (3) the recrossing transmission coefficients for R2 are 0.25, 0.38, 0.40 and 0.41 at 500, 1000, 1500 and 2000 K, respectively, but for R3 they are 0.42, 0.60, 0.64 and 0.64 respectively, and these higher recrossing transmission coefficients for R3 contribute to the higher rate constants of R3. However in most of current combustion modeling^{14-17,87}, only R2 was taken into consideration and the corresponding kinetics data have been estimated empirically, such that they have no temperature dependence. As shown in blue dotted and dashed lines in Figure 12, in the temperature range of 500-1000 K, the empirically estimated rates are a factor of 1.4-3.2 faster than our computed data.

The calculated branching fractions for R1-R6 as functions of temperature in the high-pressure limit are shown in Figure 13. The rate of reaction R7 is zero in the high-pressure limit. Figure 13 also includes the branching fractions calculated using the single-structural harmonic conventional TST rate constants. The differences are large, and they reflect the cooperative contributions of the multistructural torsional effect, the variational effect, and the multidimensional tunneling effect.

3.6 Pressure-dependent rate constants. The SS-QRRK theory²⁵, which is used for predicting the falloff effect, allows one to conveniently incorporate variational effects, tunneling, and multistructural torsional anharmonicity into the calculations of energy-resolved rate constants needed for calculating pressure-dependent rate constants, without the complexity of solving the master equation or directly calculating the input to the master equation. The pressure-dependent rate constants k_{R6} for the stabilization of P6 are plotted in Figure 14 in the temperature range of 298-2400 K. In the temperature range of 298-600 K, the deviations of the rate constants at 100 atm from the HPL are factors of 1.2-4.3; thus the falloff effect cannot be neglected even in high-pressure engines. At atmospheric pressure (1 atm), the deviations of the rate constants from the HPL are factors of 21-324 for the low-temperature range of 298-600 K. As the temperature increases, the rate constants become even farther from the high-pressure limit.

The falloff curves are plotted in Figure 15 as $\log_{10}[k(p)/k(p=\infty)]$ versus pressure, where $k(p)$ represents the rate constant of the stabilization of P6 (k_{R6}) at pressure p and $k(p=\infty)$ represents the high-pressure-limit of the rate constant. The transition pressure $p_{1/2}$ is defined as the pressure where the rate constant is half of the high-pressure-limit rate constant.⁸⁸ We obtain $p_{1/2}(T)$ by interpolation from a table of $k(T, p)$ vs. p at fixed T ; the resulting $p_{1/2}(T)$ are plotted in Figure 16. At temperatures of 300, 400, 500, and 600 K, $p_{1/2}$ is 21, 69, 158, and 339 atm respectively. However, when the temperature increases above 1000 K, $p_{1/2}$ increases rapidly with temperature. The pressure-dependent rate constants are fitted by the previously proposed formula⁸⁹ (see the SI), with a fitting error of about 20% in the ranges 298 K to 1500 K and 0.1 atm to 10 atm; the fitting parameters are tabulated in the SI.

Figure 13. In the high-pressure limit, branching fractions of R1-R6 as functions of temperature computed by (a) single-structural harmonic conventional TST and (b) MP-CVT/SCT. The branching fraction of reaction R_i is computed as the ratio of rate constant of R_i to the overall rate constant (sum of the rate constants for all reactions).

Figure 14. Computed rate constants for k_{R6} (defined as the formation of the stabilized intermediate adduct P6) as functions of temperatures at 0.01, 0.1, 1.0, 10.0, 100.0 atm and in the high-pressure-limit (HPL) respectively.

Figure 15. Predicted falloff curves for k_{R6} (defined as the formation of the stabilized intermediate adduct-P6) as a function of pressure (atm) at various temperatures.

Figure 16. The transition pressure of the stabilization of P6 (k_{R6}) as a function of temperature for Ar bath gas.

Figure 17. Rate constant of reaction R7 as a function of temperature at various pressures.

As introduced in Section 2.2, R7 is a pressure-dependent bimolecular reaction because there is a unimolecular intermediate (P6) in its reaction mechanism; the rate constants for the formation of the products P7 and CH₃COOH (k_{R7}) are plotted as functions of temperature and pressure in Figure 17. The rate constant for R7 has no pressure dependence at 800–2400 K, and over the whole temperature range studied, the rate constant for R7 is identical at 0.01 atm and 0.1 atm. However at room temperature, the rate constant for the formation of P7 + CH₃COOH at 1 atm is a factor of 5.8 larger than at 100 atm. The falloff effect is greatly influenced by the energy transfer parameters.⁶⁹ Thus we analyzed the sensitivity to Θ at various temperatures; for example the falloff curves for various Θ at 600 K are shown in Figure 18, and results at some other temperatures are provided in the SI. When Θ (and hence $\langle\Delta E\rangle_{\text{down}}$) is increased, the stabilization of P6 adduct rate constants becomes more efficient, the rate constant for R6 increases, and that for R7 decreases.

Figure 19 shows branching fractions of H abstraction, R6, and R7 as functions of temperature at 1 atm. The branching fractions at other pressures are provided in the SI. Here, H-abstraction denotes the total rate constants for all of H-abstractions (R1–R5). We can see the significant role of H-abstractions (~99%) for the overall KHP + OH kinetics at finite pressures.

Figure 18. Predicted falloff curves for reaction R6 based on using different $\langle\Delta E\rangle_{\text{down}}$ parameters.

Figure 19. Branching fractions of H-abstraction, R6, and R7 as functions of temperature at 1 atm. The branching fraction of reaction R_i is computed as the ratio of rate constant of R_i to the overall rate constant (R1–R7) and H-abstraction denotes total rate constants for all of H-abstractions (R1–R5).

Table 4. Computed standard-state entropy (cal/mol/K), heat capacity (cal/mol/K), and relative enthalpy (kcal/mol)^a for KHP using different methods

<i>T</i> (K)	<i>S</i> _T ⁰				<i>C</i> _P ⁰ (<i>T</i>)				<i>H</i> _P ⁰ (<i>T</i>)		
	MS-LH	MS-T	GA ^b	SS-HO ^c	MS-LH	MS-T	GA ^b	SS-HO ^c	MS-LH	MS-T	SS-HO ^c
298	104.3	104.6	106.6	95.7	40.7	41.2	37.7	36.0	99.9	100.1	98.5
300	104.6	104.9	106.8	95.9	40.8	41.3	37.8	36.2	99.9	100.2	98.6
400	117.4	117.7	118.5	107.6	48.5	48.1	45.4	45.3	104.4	104.6	102.7
500	129.0	129.2	128.8	118.6	55.5	54.5	51.9	53.2	109.6	109.8	107.6
600	139.7	139.6	138.0	128.9	61.5	60.1	57.5	59.8	115.5	115.5	113.3
700	149.5	149.2	146.3	138.5	66.6	64.9	62.3	65.2	121.9	121.8	119.5
800	158.7	158.2	153.5	147.6	70.9	68.9	66.4	69.8	128.8	128.4	126.3
900	167.3	166.5	159.8	156.0	74.6	72.3	69.8	73.7	136.1	135.5	133.5
1000	175.3	174.3	165.3	164.0	77.8	75.3	72.8	77.1	143.7	142.9	141.0

^aZero of energy is set to potential energy of global minimum;

^bCalculated by using the Benson's group additivity (GA) method.

^cCalculated using the lowest-energy equilibrium conformer.

Table 5. Averaged generalized transmission coefficient^a of reactions R1-R5

<i>T</i> (K)	R1			R2			R3			R4			R5		
	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_2$	$\langle\gamma\rangle_4$	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_2$	$\langle\gamma\rangle_4$	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_2$	$\langle\gamma\rangle_4$	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_2$	$\langle\gamma\rangle_4$	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_2$	$\langle\gamma\rangle_4$
298	0.97	0.50	0.86	0.12	0.12	0.13	0.24	0.23	0.25	0.25	1.11	1.06	0.52	0.59	0.61
400	0.64	0.29	0.59	0.19	0.18	0.19	0.34	0.32	0.34	0.28	0.80	0.76	0.46	0.56	0.54
600	0.76	0.99	0.82	0.29	0.26	0.27	0.48	0.42	0.44	0.33	0.68	0.63	0.46	0.55	0.53
800	0.81	0.94	0.79	0.34	0.29	0.30	0.56	0.47	0.49	0.36	0.64	0.59	0.46	0.57	0.53
1000	0.83	0.93	0.78	0.38	0.31	0.32	0.60	0.50	0.52	0.37	0.61	0.56	0.47	0.59	0.54
1500	0.86	0.92	0.77	0.40	0.32	0.33	0.64	0.51	0.53	0.38	0.56	0.51	0.46	0.60	0.53
2400	0.87	0.93	0.76	0.41	0.31	0.33	0.64	0.51	0.53	0.37	0.50	0.44	0.45	0.61	0.52

^aThe generalized transmission coefficient averaged over the first *P* paths is defined as $\langle\gamma\rangle_P$ by eq 3.

3.7 Implication for KHP chemistry. It is essentially impossible to detect the H-abstraction reactions experimentally. First, the preparation and purification of KHP is a complex process. Second, storage is difficult because KHP is very active. Third, these H-abstraction reactions can produce different products such as P1, P2, P3, P4, and P5, which are reactive radicals. Therefore theoretical calculations are essential for understanding these H-abstraction reactions and their branching fractions.

The products of the reactions studied here can dissociate into diones, cyclic ethers, or olefenic ketones via the loss of OH and HO₂ radicals. These products have been detected experimentally in *n*-pentane oxidation,¹⁴ and the present kinetics data may enable their more accurate inclusion in ignition modeling and atmospheric modeling. For example, the product of reaction R2 is an unstable hydroperoxy radical that will immediately decompose to pentadione plus an OH radical. This prompt liberation of an OH radical is important kinetically in both atmospheric and pre-ignition chemistry.

Recent experimental work by Wang et al.⁹⁰ studied the auto-oxidation of *n*-heptane. In addition to the carbonyl

hydroperoxide (C₇H₁₄O₃, abbreviated as C₇-KHP), they detected mass peaks corresponding to C₇H₁₂O₂ and C₇H₁₂O species. They proposed that these intermediates could be produced from the H-atom abstraction of carbonyl hydroperoxide by OH radical. A possible structure of the C₇H₁₂O₂ species is a C₇ dione and/or a keto cyclic ether (e.g., with one carbonyl and one cyclic ether group); a possible structure of C₇H₁₂O is a heptenone. This experiment detection highlights the significant role in determining the formation of diones, alkenones, and keto cyclic ethers through H-atom abstraction of carbonyl hydroperoxides. A consequence of the present work is that C₅ diones and/or keto cyclic ethers (i.e., C₅H₈O₂) and pentenones (i.e., C₅H₈O) can result from the H-atom abstraction of KHP, as shown in Figure S9 of the SI. To study this further, we selected one of the carbonyl hydroperoxides from *n*-pentane auto-oxidation to study H-atom abstraction reactions by OH radical.

In the original *n*-pentane kinetic model by Bugler et al.,¹⁷ the reaction pathways for KHP + OH were not taken into consideration. To study the effect of these reactions, we updated the KHP mechanism in the original *n*-

pentane kinetic model of Bugler et al.¹⁷ by considering our new KHP + OH rate constants, and we carried out a simulation with the updated mechanism. The subsequent reactions of the carbonyl hydroperoxide radicals, via β -C-O scission, β -O-O scission, cyclization, and concerted elimination, lead to $C_5H_8O_2$ intermediates (e.g., in the notation of Fig. S9, these are P1-2, P2-1, P4-1, and P5-1) and C_5H_8O intermediates (e.g., P1-1 and P3-1). For the simulation, we required thermodynamic data for the new species in Figure S9 of the SI, and these data were estimated by THERM⁹¹ to be consistent with the original model. The detailed model information for our simulation is provided in the SI.

The simulation was performed by using the CHEMKIN-PRO software⁹² using the perfect stirred reactor module. The input for the simulation is as follows: residence time⁹³ (which is defined as the ratio of the reactor volume and the volume flow rate of the gas flowing through the reactor) is set to be 2 s, the pressure is 40 bar, the *n*-pentane mole fraction is 10000 ppm, the equivalence ratio (which is defined as the actual air fuel ratio divided by the air fuel ratio for complete combustion) is 0.4, and the dilution gas is N_2 . We investigated the temperature range of 500–650 K.

To learn the effect of the new rate constants on the products, we performed two simulations. In one, we updated the original *n*-pentane model¹⁷ by adding our new calculated rate constants of R1-R5. In the other, we only added R2 with an estimated rate constant of $1.67 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (taken to have no temperature dependence), which is the value used in a previous reference.¹⁹ Results from these two simulations are compared in Figure 20. Figure 20(a) shows that the H-abstraction reactions of KHP by OH radical and the subsequent reactions in Figure S9 of the SI produce several $C_5H_8O_2$ and C_5H_8O intermediates. The highest-yield C_5H_8O isomer is a pentenone (i.e., P3-1) produced through pathways R3 and R4. The formation mole fractions of 2,4-pentanedione (i.e., P2-1) and a pentenone (i.e., P1-1) are comparable with the formation of P3-1. In contrast, the mole fractions of C_5 keto cyclic ethers (i.e., P1-2, P4-1, and P5-1) are much lower. In Figure 20(b), the mole fraction of 2,4-pentanedione (P2-1) is five times higher than that in Figure 20(a). One of the main reasons is that the rate constant of R2 recommended by Bugler et al.¹⁹ is much higher than our calculation result in present work. The simulation we have just presented indicates that the new H-abstraction reaction rates for reactions of KHP with OH lead to observable changes in the predicted production of downstream products in conditions related to auto-ignition. On the other hand, differences in reaction rate constants for the H-atom abstraction reactions at different sites of KHP lead to a particular distribution of final products (P1-1, P1-2, P2-1...), which are not distinguished by current experimental diagnostics.

Although we performed high-level calculations for rate constants, directly using our results in a previously constructed combustion model will not necessarily lead to better agreement with experimental signals (such as final

product distribution or ignition delay times), because of the uncertainty of the rate constants for other reactions that were previously added in the model, especially if the model contains some rate constants that were previously adjusted empirically to match the experimental data points.⁹⁴ Nevertheless, the process of gradually adding more reliable data to the models should in the long run produce more reliable models of combustion.

Figure 20. Mole fraction profiles of $C_5H_8O_2$ species (in particular P1-2, P2-1, P4-1 and P5-1) and C_5H_8O species (in particular P1-1 and P3-1) during *n*-pentane auto-oxidation in a jet-stirred reactor at 40 bar. (a) Simulation with updated KHP mechanism by adding our new calculated rate constants of R1-R5 to the original *n*-pentane model;¹⁷ (b) simulation by only adding Ref. 19's estimated rate constant of R2 (without adding other reactions) to the original KHP mechanism of Bugler et al.¹⁷

In the atmosphere, the products of the reactions studied here are expected to further associate with O_2 , which may contribute to the formation of secondary organic aerosols (SOA) via the formation of low-volatility organic compounds.

It would be interesting to investigate the reactions of other hydroperoxides with OH to learn how the rate constants vary. As a preliminary step in this direction, we calculated the classical energy barriers for reaction of OH with some simpler hydroperoxides. The formulas of the

investigated molecules are $\text{HOOCH}_2\text{CH}_2\text{CHO}$, which is called C_3 , $\text{HOOCH}_2\text{CH}_2\text{C(=O)CH}_3$, which is called C_{4-1} , and $\text{CH}_3\text{CH(OOH)CH}_2\text{CHO}$, which is called C_{4-2} . The detailed results are in Figs. S5–S7 of the SI, and they show the same trends as for the KHP investigated in the present work, which is 4-hydroperoxy-2-pentanone. In particular the H-atom on the carbon bonded to the OOH group is the preferred reaction site, followed by the OOH group, and the least favorable abstraction site is the H-atom on the CH_3 group adjacent to the carbonyl group. The absolute values of energy barriers vary by about 1 kcal/mol for the various hydroperoxides, e.g. for our KHP, as shown in Table 1, the energy barriers for TS2 and TS3 are -4.76 and -2.73 kcal/mol, and for C_{4-2} , the corresponding energy barriers are -4.31 and -2.25 kcal/mol respectively. Comparing KHP with C_{4-1} , the differences for R2, R3, and R4 are no larger than 0.18 kcal/mol, but the barrier for abstraction of the H-atom on the carbon bonded to OOH group is 0.61 kcal/mol higher for C_{4-1} due to the electronic effect of CH_3 group. Our calculations on these small hydroperoxides with OH indicate that the general conclusions of the present work can be applied rather generally to the degradation of carbonyl hydroperoxides.

4. CONCLUSIONS

In this work, multipath and multistructural canonical variational transition-state-theory with small-curvature tunneling are used to calculate high-pressure-limit rate constants for hydrogen abstraction of ketohydroperoxide by hydroxyl radical, and the pressure-dependent rate constants have been computed for the addition reactions using the SS-QRRK method. Our calculations include accurate determinations of the classical barrier heights, the variational effects, internal-coordinate-based vibrationally adiabatic potentials, multistructural torsional anharmonicity, and multidimensional tunneling effects as put together by multipath VTST.

We found that multistructural anharmonicity has a large effect on the thermodynamic data, and it changes the rate constants by factors of 0.2 to 12. The variational effect plays an important role in the determination of the rate constants, and it may be as large as a factor of 10 at low temperatures. We also found that the tunneling effect is large and cannot be ignored, e.g., the tunneling coefficient on reaction R4 (Boltzmann-averaged over four paths) is 4 at 298 K and 10 at 250 K.

We find that R2 and R3 are the dominant reactions, and R3 is faster than R2 even though R2 has the lowest energy barrier. This result reflects the crucial role of variational effects and multistructural torsional anharmonicity, and the details of the present calculation show the importance of including these effects in combustion and atmospheric modeling.

The accurate thermodynamic and kinetics data computed in this work should be valuable for improving the accuracy of chemical kinetics models for alkane oxidation and the global modeling of secondary organic aerosols.

ASSOCIATED CONTENT

Supporting Information

Mean unsigned error of various tested electronic structure methods, barrier heights, reaction energies, thermodynamic data, partition functions, and fitting parameters, Cartesian coordinates and absolute energies, pathways analysis for the subsequent fate of products (P1–P5), fitting formula and fitting parameters for the pressure-dependent rate constants of R6 and R7, local periodicity values, the eleven highest and eleven lowest vibrational frequencies, predicted falloff curves for reaction R6 using different $\langle\Delta E\rangle_{\text{down}}$ parameters, branching fractions as functions of temperature and pressure, H-abstraction reaction mechanism of KHP + OH, comparison of energy barriers between our KHP+OH reaction and some other small hydroperoxides (C_3 and C_4) reacting with OH. Input file for the CHEMKIN simulation.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/

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Notes

The authors declare no competing financial interest.

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