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Hydrogen shift isomerizations in the kinetics of the second oxidation mechanism of alkane combustion. Reactions of the hydroperoxypentylperoxy OOQOOH radical[☆]

Lili Xing[a,b,1,*], Junwei Lucas Bao[b,1], Zhandong Wang[c], Xuetao Wang[a], Donald G. Truhlar[b]

[a] *Energy and Power Engineering Institute, Henan University of Science and Technology, Luoyang, Henan 471003, China*
[b] *Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, MN 55455-0431, USA*
[c] *King Abdullah University of Science and Technology, Clean Combustion Research Center, Thuwal 23955-6900, Saudi Arabia*

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ABSTRACT

Hydroperoxyalkylperoxy species are important intermediates that are generated during the autoignition of transport fuels. In combustion, the fate of hydroperoxyalkylperoxy is important for the performance of advanced combustion engines, especially for autoignition. A key fate of the hydroperoxyalkylperoxy is a 1,5 H-shift, for which kinetics data are experimentally unavailable. In the present work, we study 1-hydroperoxypentan-3-yl)dioxidanyl ($CH_3CH_2CH(OO)CH_2CH_2OOH$) as a model compound to clarify the kinetics of 1,5 H-shift of hydroperoxyalkylperoxy species, in particular α-H isomerization and alternative competitive pathways. 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 computed by conventional single-structure harmonic transition state theory (TST) and than the empirically estimated rate constants that are currently used in combustion modeling. The roles of various factors in determining the rates are elucidated. The pressure-dependent rate constants for these competitive reactions are computed using system-specific quantum RRK theory. The calculated temperature range is 298–1500 K, and the pressure range is 0.01–100 atm. The accurate thermodynamic and kinetics data determined in this work are indispensable in the detailed understanding and prediction of ignition properties of hydrocarbons and alternative fuels.

1. Introduction

The autoignition of hydrocarbons is of central importance to combustion chemistry [1,2]. A key issue is the competition between radical chain propagation and branching versus chain termination [3–6]. This competition depends critically on the fate of peroxy radicals (ROO, where $R = C_nH_{2n+1}$), hydroperoxyalkyl radicals (QOOH, where $Q = C_nH_{2n}$), and hydroperoxyalkylperoxy radicals (OOQOOH) [3,5,6]. In the low-temperature autoignition chemistry of alkanes, the presence of many of the involved species, such as hydroperoxyalkyl radicals (QOOH) [7], large alkenes [8-10], cyclic ethers [8,11,12], and ketohydroperoxides (KHPs) [13–17], has been confirmed by experimental detection. The OH profiles in previous studies suggest the occurrence of a second oxidation, i.e., $O_2 + QOOH \rightarrow OOQOOH$ [18]. Scheme 1 shows the resulting reaction mechanism, which involves the isomerization of the OOQOOH. The most favorable isomerization path is usually assumed to be the transfer of an H from the carbon attached to the hydroperoxyl group [19]; it is conventional to label this site as α and to call this an α-H shift. This yields HOOQ′OOH (where $Q' = C_nH_{2n-1}$), and this radical can decompose to yield more OH radicals, resulting in chain branching.

However, there has never been any experimental detection of an OOQOOH species, and therefore accurate thermodynamics and kinetics data are missing. Some models that have been used assumed that the rate constants for OOQOOH isomerization can be obtained from those for ROO isomerization by applying a 3–4 kcal/mol correction to the activation energy to account for the weaker C–H bond on Q as compared to R [20].

It is also possible for a hydrogen atom to migrate from another site of OOQOOH. Some recent studies have included alternative competitive reaction pathways for OOQOOH [19,21,22]. The

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[*] Corresponding author at: Energy and Power Engineering Institute, Henan University of Science and Technology, Luoyang, Henan 471003, China.

E-mail address: xingll2018@haust.edu.cn (L. Xing).

[1] These authors contributed equally.

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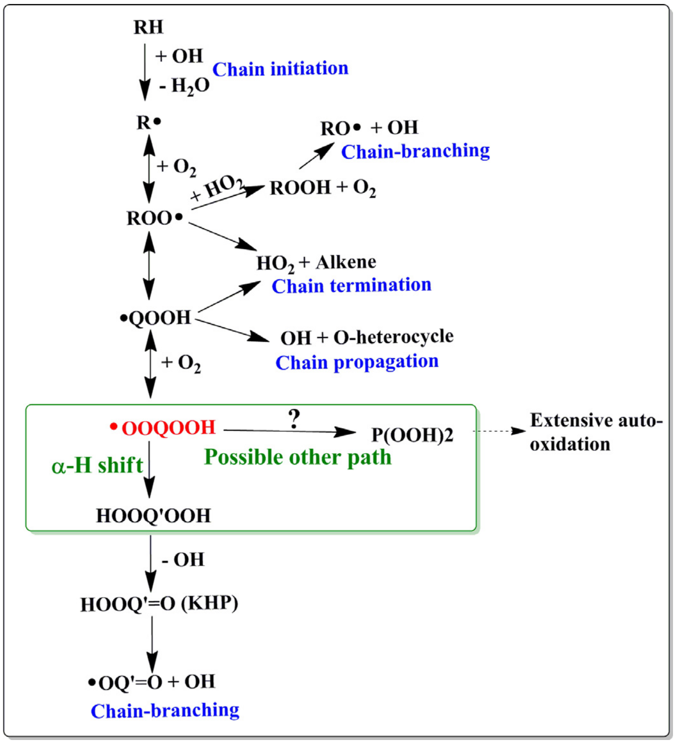
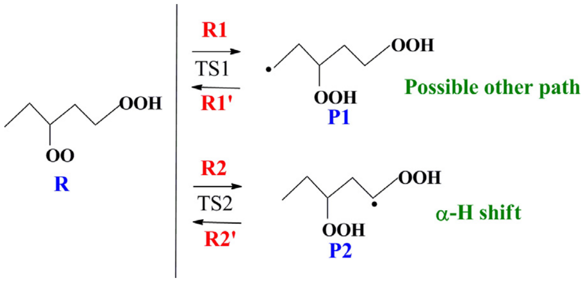


Scheme 1. Simplified low-temperature oxidation mechanism.



Scheme 2. A prototypical OOQOOH radical (1-hydroperoxypentan-3-yl)dioxidanyl) and its correspongding reaction pathways of 1,5 H-shift.

competition between α-H isomerization reactions and alternative isomerizations has a large effect on the extent of auto-oxidation and the possible production of highly oxygenated intermediates [23]. Silke et al. [24] found that including alternative pathways leads to longer ignition delay due to a high concentration of the HO_2 radicals produced at temperature below ~830 K. Mohamed et al. [20] added a new alternative isomerization pathway in a model of 2-methylhexane oxidation model and found that the reactivity is thereby predicted to increase. Wang et al.'s work provides experimental evidence that highly oxygenated intermediates with one or more hydroperoxy groups are prevalent in the auto-oxidation of various oxygenated organic compounds [23]. However, Bugler et al. [25] found that alternative pathways have little effect on the overall reactivity. The results clearly depend on the precise identity of the alkane being oxidized, and the quality of the theoretical predictions for the various cases is difficult to assess. More work is needed on the thermodynamics and kinetics to quantify the effect of $O_2 + QOOH$ chemistry on chain branching.

The competition between possible isomerization must consider not only the difference in bond energies of H bonded at various distances from a radical site, but also the difference in bond strengths of C–H bonds at primary, secondary, and tertiary carbons and the size of the ring in the transition state (TS) for H transfer. Here we consider two of the reactions involved in oxidation of pentane to investigate the kinetics of hydrogen shift reaction pathways. The initial formation of n-pentylperoxy radicals (ROO) yields a significant amount of 1- hydroperoxy-3-pentyl radical (which is a γ-QOOH species) via 1,5 H-shift. After a second O_2 addition, this yields a hydroperoxypentylperoxy radical (in particular, 1-hydroperoxypentan-3-yl)dioxidanyl, which is an OOQOOH species). Scheme 2 shows this OOQOOH radical and two of its isomerization pathways that are both 1,5 H-shifts – thus both reactions have six-membered rings in the H-transfer transition state. (We do not consider the two possible 1,4 H-shifts that have a five-membered-ring transition state.) In the rest of this article, we let **R** denote the OOQOOH species of Scheme 2; and we label 3,5-dihydroperoxy-n-pentyl ($\bullet CH_2CH_2CH(OOH)CH_2OOH$) as **P1** and 1,3-dihydroperoxy-n-pentyl ($CH_3CH_2CH(OOH)CH_2C\bullet HOOH$) as **P2**.

For a chain molecule like **R**, there are many conformers due to internal rotation, but the number of conformers decreases in hydrogen-shift TSs due to the ring structures of the TSs. Thus the overall transition state partition function is usually smaller than that of the reactant, which decreases the rate constants. To calculate this effect accurately one should use a method capable of treating coupled torsions [19,26], and we do that here. We compute the potential energy surfaces for both isomerizations, and we use multipath variational transition state theory (MP-VTST) with multidimensional tunneling contributions to compute the rate constants. These rate calculations include multiple-structure anharmonicity and torsional potential anharmonicity. To estimate the pressure effects, we use system-specific quantum Rice–Ramsperger–Kassel (SS-QRRK) theory [27] with the thermal activation mechanism [28–30] to compute the thermal rate constants as functions of pressure. The thermal activation mechanism assumes that OOQOOH is thermally equilibrated before it reacts (as opposed to reaction of hot nascent molecules, which would be the chemical activation mechanism).

2. Theoretical background

In this section, we briefly review the methods we applied in this work.

2.1. Multistructural method with torsional anharmonicity

Torsions can generate multiple conformers (also called structures); for reactants and products they are local minima, and for transition states they are saddle points. We used the multistructural method with coupled torsional-potential anharmonicity [31–34] (MS-T) to calculate the partition functions as functions of temperature, and we included all the inter-convertible torsional conformers into consideration. The conformational-vibrational-rotation partition function at temperature T of the given species (reactant, product, or transition state) with J distinguishable conformers and t torsions is

$$Q^{\mathrm{MS-T}}_{\mathrm{con-rovib}} = \sum_{j=1}^{J} Q_j^{\mathrm{SS-T}} \tag{1}$$

$$Q_j^{\mathrm{SS-T}} = Q_{\mathrm{rot},j}\exp\left(-\frac{U_j}{k_B T}\right) Q_j^{\mathrm{QH}} \prod_{\tau=1}^{t} \widetilde{f_{j,\tau}} \tag{2}$$

where j denotes a conformer, $Q_{\mathrm{rot},j}$ is the classical rotational partation function of conformer j including the symmetry number for overall rotation (these symmetry numbers are unity for all cases in this article), U_j is the relative potential energy when the local minimum of the potential energy surface for the calculation of the partition function of a given species is chosen as the local zero of energy, k_{B} is the Boltzmann constant, Q_j^{QH} is the quasiharmonic (QH)