



Ab initio kinetics on low temperature oxidation of *iso*-pentane: The first oxygen addition

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ABSTRACT

The chemistry of R+O₂ reaction in the low temperature oxidation of *iso*-pentane has been investigated by using quantum chemical calculations coupled with RRKM/master-equation simulations. All the four independent C₅H₁₁ radicals of the *iso*-pentane molecule were included in the investigation, i.e., 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl and 1,1-dimethylpropyl. The major reaction channels were explored in great detail, and the rate constants of key reactions were provided at high pressure limit and the falloff region. The QOOH radicals generated in R+O₂ reactions, which are of particular importance to subsequent chain-branching, are explicitly identified. For these QOOH radicals, the buildup of concentration is typically attributed to the combined effect of the rapid equilibration with preceding alkylperoxy radical and the absence of fast dissociation channels. In addition, these QOOH radicals are all formed from isomerization of RO₂ via six-member ring transition states, demonstrating the great significance of 1,5 H-transfers in the low temperature oxidation of alkanes. This work provides useful data for kinetic modeling of low temperature combustion for surrogate fuels and can be used as a starting point for the study about the reaction kinetics of the second oxygen addition in higher alkanes.

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1. Introduction

Low temperature combustion is at the core of technologies for advanced engine concepts. Unlike traditional combustion engines, the new engine types are rather sensitive to the fuel chemistry. As such, a fundamental understanding of low temperature combustion chemistry is very crucial for the design and improvement of new engines [1]. Kinetic modeling serves as a useful tool in utilizing the fundamental reaction mechanism to evaluate the engine-relevant behaviors of fuels, such as ignition properties and pollutant formation. Given the urgent demands for modeling practical combustion problems, the core reactions in the mechanism must be provided with reliable kinetic data that cover different conditions, i.e., temperature, pressure and mixture-composition.

The reactions of alkyl radicals with oxygen are one type of reactions that are of the utmost significance at the inception phase of low temperature oxidation of alkanes [1]. These reactions, generally referred to as the first O₂ addition, are often represented as R+O₂. The alkyl radical, R, reacts with O₂ and forms the energetically excited alkylperoxy radical, RO₂^{*}. This excited adduct can

stabilize via unreactive collisions, decompose to fragmented products, or isomerize to hydroperoxyalkyl (QOOH) via intramolecular H-transfers. The QOOH radical can proceed by C–O or O–O fissions to form HO₂+alkene or OH+cyclic ether. The formation of OH is very important for the ignition chemistry, but the more important aspect of the isomerization reaction, RO₂→QOOH, is the transient QOOH species itself. With the unpaired electron located at a carbon atom, QOOH can further undergo a second O₂ addition to form the hydroperoxyalkylperoxy radical (OOQOOH), which can isomerize and eventually dissociate to OH+OH+oxy-radical or HO₂+OH+oxy-radical. This second O₂ addition is often represented as O₂+QOOH.

Looking again into the scenarios above, it emerges that in the first O₂ addition one radical is generated for every one radical consumed, that is, the number of radicals remains equal. The R+O₂ reaction is therefore chain propagating. In contrast, in the second O₂ addition three radicals are generated for every one radical consumed, making O₂+QOOH chain branching. The second O₂ addition is commonly believed to be responsible for the exponential growth in radical concentration during ignition of hydrocarbon oxidation [2]. For this reason, the QOOH species are central to the low temperature oxidation chemistry and their concentrations should accumulate sufficiently high for the O₂+QOOH chemistry to become significant.

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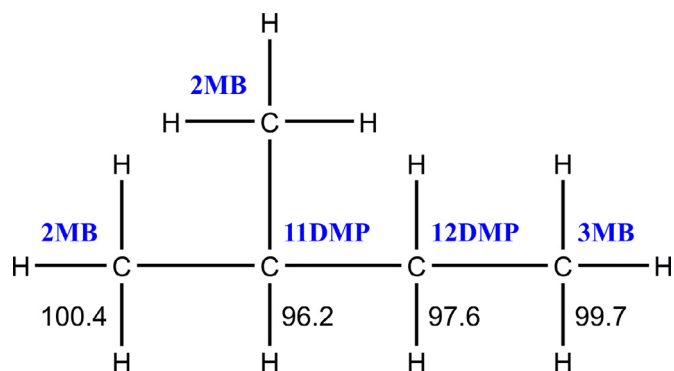


Fig. 1. Schematic structure and C–H bond dissociation energies at 0 K in kcal/mol of the *iso*-pentane molecule using the method scheme in Section 2.1. The blue labels are abbreviations of radical names after H-loss from designated carbon atoms of *iso*-pentane. 2MB is short for 2-methylbutyl, 3MB for 3-methylbutyl, 12DMP for 1,2-dimethylpropyl, and 11DMP for 1,1-dimethylpropyl. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Branched alkanes are one of the most abundant compositions in practical fuels, such as gasoline, diesel, and jet fuels. Take gasoline for instance. Branched alkanes constitute the largest part of the USA gasolines, and a typical European gasoline usually contains branched alkanes with a composition of over 30% [3]. As a result, surrogate fuels used to develop kinetic models normally include branched alkanes as an essential component. With respect to the low temperature oxidation of alkanes, previous studies about reaction mechanism are mostly centered on C2–C4 alkanes [4–12]. Much less studies were found for C5 and higher alkanes [13–16]. Specifically for *iso*-pentane, only very limited reaction kinetic data is available [16,17]. Thermodynamic and kinetic parameters for key elementary reactions in low temperature oxidation are rather difficult to obtain directly from experimental measurements. Theoretical methods, therefore, serve as a powerful tool for exploration into detailed chemistry of complex reaction systems and for interpretation of diverse experimental phenomena in hydrocarbon oxidation. Relevant computational studies on larger alkanes are very challenging because of the presence of more reactive sites, which greatly adds the complexities of reaction network and dramatically increases the computational expense.

In present work, *iso*-pentane is chosen as the target molecule for the first O₂ addition mechanism in the low temperature oxidation. *iso*-Pentane can act as a bridge between small alkanes and alkanes of larger size. Its reaction mechanism can be used as a reference in practical modeling of higher alkanes. Figure 1 shows the schematic structure of the *iso*-pentane molecule. The labels are used to represent the radicals formed via one H-loss from designated carbon atoms. Specifically, 2MB is short for 2-methylbutyl, formed via H-loss from primary carbon atom; 3MB is short for 3-methylbutyl, formed via H-loss from another primary carbon atom; 12DMP is short for 1,2-dimethylpropyl, via H-loss from secondary carbon atom; and 11DMP is for 1,1-dimethylpropyl, via H-loss from tertiary carbon atom. The bond dissociation energies of C–H are displayed at 0 K in kcal/mol using the QCISD(T)/CBS//B3LYP/6-311++G(d,p) scheme presented in Section 2.1. From the C–H bond dissociation energies, it is easier to abstract a hydrogen atom from the secondary and tertiary carbons than from the primary carbons. The thermodynamic distribution no longer applies for the population of initially formed C₅H₁₁ radicals. Other factors, such as the abstracting radical, also affect the C₅H₁₁ population. Also, considering that there are more equivalent H atoms at the primary carbons, the initial hydrogen abstractions from *iso*-pentane essentially yield significant amounts of all the four C₅H₁₁ radicals.

One important aspect of this work is the exhaustive exploration of the potential energy surfaces for the reactions of molecular oxygen with various C₅H₁₁ radicals. Another key aspect lies in the ab initio RRKM/master-equation predictions of rate coefficients for core reactions in the first oxygen addition process at high pressure limit and the falloff region. Particularly, significant QOOH radicals that are expected to play an important role in second oxygen addition are explicitly identified.

2. Quantum chemical calculations

2.1. Potential energy surfaces

The B3LYP/6-311++G(d,p) level [18] was employed for geometry optimization and frequency analysis of stationary points on C₅H₁₁O₂ potential energy surfaces. The transition states were identified by having one and only one imaginary frequency, and were verified to correspond to the desired reaction coordinate through vibrational mode animation. For ambiguous cases, the intrinsic reaction coordinate (IRC) analysis [19] was performed to ensure the correct connectivity of transition states to designated reactants and products.

To refine the energies, higher level corrections were computed at B3LYP geometries using QCISD(T) method with cc-pVDZ and cc-pVTZ basis sets. The complete basis set (CBS) limit was extrapolated from the double- and triple- ζ basis set calculations by applying the inverse power law assumption [20]

$$E_{\text{CBS}}^{\text{QCI}} = E_{\text{TZ}}^{\text{QCI}} + (E_{\text{TZ}}^{\text{QCI}} - E_{\text{DZ}}^{\text{QCI}}) \frac{3^4}{4^4 - 3^4} \quad (\text{E1})$$

In Eq. (E1), DZ and TZ are abbreviations of cc-pVDZ and cc-pVTZ basis sets, respectively. The zero point vibrational energies were included from the B3LYP frequency analysis.

2.2. Entrance channel of O₂ addition

The nature of triplet ground-state renders molecular oxygen reactive like a radical in the entrance channel of R + O₂ reactions. These reactions are typically barrierless, or otherwise have a very flat energy maximum in some few cases. Interaction potential between the two moieties is often desired in order to quantify the minimum reactive flux through the transition state region. Two density functional (DFT) methods, M062X and B3LYP, were tested for the mapping of the interaction potentials. The test result shows that these two methods failed to acquire a smooth energy change along the reaction coordinate, implying that single-reference methods are probably inappropriate for this process.

The multi-reference method, CASSCF(7e,5o)/cc-pVDZ, was then used to perform the relaxed scan along the reaction coordinate. Frequencies were also obtained with the same level. After that, the MRCI(7e,5o) energies at cc-pVDZ and cc-pVTZ basis sets were computed and extrapolated to the CBS limit using a formula similar to (E1), with the Davidson correction included. In particular, the (7e,5o) active space consists of one electron in one orbital for the carbon-centered radical and six electrons in four orbitals for molecular oxygen. The CBS limit energies obtained above were scaled by reference to the asymptotic energies of the R + O₂ = RO₂ reaction achieved via the QCISD(T)/CBS//B3LYP/6-311++G(d,p) scheme. Note that the radical-radical interaction potentials at the CASSCF level are normally less attractive due to the neglect of dynamical correlation effects, compared to the potentials by more rigorous methods such as CASPT2 and MRCI [21]. As a result, the energies at transition state region of the entrance channels were varied and tested in practical kinetic calculations in order to achieve the most appropriate rate coefficients.

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