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Theoretical study on the thermal decomposition and isomerization of 3-Me-1-heptyl radical

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ABSTRACT

A detailed theoretical investigation on the thermal decomposition and isomerization of 3-Me-1-heptyl radical is performed at the *ab initio* CBS-QB3 level of theory. The calculation reveals that the detailed reaction mechanisms of 3-Me-1-heptyl radical mainly incorporate reversible intramolecular hydrogen atom transfer and the beta-site C—C bond scission. The standard reaction enthalpies ($\Delta_r H^0_{298}$) and enthalpies of formation ($\Delta_f H^0_{298}$) are determined at the CBS-QB3 level of theory. All investigated decomposition reactions are generally endothermic, while most of the isomerization processes are exothermic. Among the hydrogen atom transfer processes, the 1,3- and 1,2-hydrogen atom migration (R_5 and R_6, respectively) are prohibited due to their high isomerization barriers, while the 1,6-(R_2) and 1,5-hydrogen atom transfer (R_3) are kinetically accessible (owing to their low ring strains in the cyclic transition states). Compared with the 1,5-hydrogen atom shift for the *n*-heptyl radical, the methyl-substitution increases the rate coefficient by a factor of about 3.0. The product distributions are predicted at different temperatures on the basis of the steady-state approximation (SSA). The ultimate and dominant products majorly include ethylene (C_2H_4), propylene (C_3H_6), 1-butylene (1-C_4H_8) and 2-hexene (2-C_6H_{12}) over the temperature range of 500–2500 K.

1. Introduction

The branched-chain alkanes are one of the most important classes of fossil fuel [1], so the detailed reaction mechanisms and thermochemical properties of these molecules and their corresponding radicals have been concerned experimentally and theoretically [2–6]. Alkyl radicals are the key intermediates formed during the thermal decomposition processes of hydrocarbons, resulting from the C—H bond scission or hydrogen abstraction by some small radicals. These metastable alkyl radicals readily decompose into smaller radicals and olefin at elevated temperatures. Among them, the 3-Me-1-heptyl radical, which can derive from CH_3 group substitution on *n*-heptyl radical, serves as an important intermediate in hydrocarbon combustion and pyrolysis chemistry. A detailed knowledge of its thermochemical and kinetic characters is important to improve our understanding on the thermal decomposition processes of the branched-chain alkanes.

To the best of our knowledge, no experimental studies on the thermal decomposition of 3-Me-1-heptyl radical have been reported so far. Such a metastable and highly-reactive radical is difficult to be characterized experimentally [7]. In 2010, Awan et al. [1] studied the thermal decomposition and isomerization of the 5-Me-1-hexyl radical by mean of the single pulse shock tube technique at temperatures of 889–1064 K and pressures of 1.6–2.2 bar. The kinetics and reaction mechanisms are deduced by gas chromatographic analysis of the products. They found that the major pyrolysis products of 5-Me-1-hexyl radical involve ethene (C_2H_4), propene (C_3H_6), isobutene (2-Me-1-C_3H_5), 1-butene (1-C_4H_8), 1-hexene (1-C_6H_{12}) etc, and among them the first three products account for as much as 90% of the carbon balance. Curran et al. [8] investigated the oxidation of iso-octane molecule (i-C_8H_{18}) in a jet-stirred reactor, flow reactors, shock tubes and a motored engine at temperatures of 550–1700 K and pressures of 1–45 atm. They proposed a detailed chemical kinetic mechanism for i-C_8H_{18} oxidation, which has been validated by using ignition behind reflected shock waves at both low and high temperatures. Both of experimental works provide valuable information for understanding the detailed reaction mechanism of 3-Me-1-heptyl radical. However, the rate coefficients for the secondary reactions of these formed radicals are difficult to be determined experimentally with a satisfactory accuracy or are lacking entirely.

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Theoretically, the detailed mechanisms, thermochemical and kinetic properties of 3-Me-1-heptyl radical have not been reported. Recently, Ding et al. [9] investigated the pyrolysis of *n*-heptane by molecular dynamic simulations based on a series of reactive force field (ReaxFF) at high temperature. The calculated results indicated that the entire pyrolysis process of *n*-heptane was radical dominated, and the unimolecular dissociation was a principal pathway. Viskolcz et al. [2] studied a series of isomerization reactions for 2-Me-1-hexyl radical from 1,2- to 1,6-hydrogen atom migration, without considering these isomers decomposition processes. They found that in all isomerization pathways, the fastest one is the 1,5-hydrogen atom transfer which proceeds through a six-membered cyclic transition state. All these investigations offer insight to the detailed reaction mechanisms of alkane molecules and their radicals. Unfortunately, the direct decomposition processes of these isomers and the final product distributions have not been taken into consideration in Viskolcz's study [2].

In the current work, a systematically theoretical investigation about the thermal decomposition and isomerization of 3-Me-1-heptyl radical is carried out as follows: Firstly, the detailed reaction mechanisms, including the reversible intramolecular hydrogen atom migration and the beta-site C—C bond cleavage processes, are explored. Secondly, the optimized geometries of all stationary points, standard reaction enthalpies ($\Delta_r H^0_{298}$) and enthalpies of formation ($\Delta_f H^0_{298}$) are determined by using the high-level composite CBS-QB3 approach. Thirdly, the high-pressure limit (HPL) rate coefficients of conventional transition state theory for individual elementary reaction are evaluated at 500–2500 K. Finally, the product distributions are predicted at different temperatures on the basis of the steady-state approximation. The computational results, along with detailed discussions, will be presented in Section 3 and main conclusions will be drawn in Section 4.

2. Theoretical and computational methods

All the electronic structure calculations are carried out utilizing the Gaussian 09 package of programs [10]. Geometric parameters are visualized with GaussView 5.0 [11]. The equilibrium geometries for open-shell species are determined with an unrestricted density functional theory (UB3LYP) in conjunction with 6-311G(2d,d,p) basis set, as denoted with a "U" prefix, while the closed-shell species are performed using a restricted functional by default, as denoted with a "R" prefix (For simplicity, the prefix "U" and "R" are omitted in the subsequent discussions). Vibrational frequency calculations are employed to identify the stationary points (in which minima have no imaginary frequencies and transition states have only one). Intrinsic reaction coordinate (IRC) calculations [12–15] are traced at the same level of theory to confirm that the located transition state indeed connect to the designated reactants and products. Then, to obtain reliable energies of each species on the potential energy surface (PES), the single point calculations are performed by using the CBS-QB3 procedure [16] at the geometry obtained from the B3LYP/6-311G(2d,d,p) level. Such situation was observed in Sirjean's study [5] for the isomerization processes of *n*-alkyl radicals. The CBS-QB3 procedure is outlined as follows: Firstly, geometry optimizations and frequency calculations (scale by 0.99 as recommended by Montgomery et al. [16]) at B3LYP/6-311G(2d,d,p) level [17]. Secondly, the singlet point calculations at the CCSD(T)/6-31+G(d′), MP4SDQ/CBSB4 (CBSB4 = 6-31+G(d(f),p)), MP2/CBSB3 (CBSB3 = 6-311+G(3d2f,2df,2p)) levels, respectively. Finally, a complete basis set (CBS) extrapolation to correct the total energy [18]. Numerous previous investigations have proposed that the CBS-QB3 method provides adequately accurate energies for C/H/O system, with a standard deviation of about 1.5 kcal mol^{-1} [19–21]. Meanwhile, it is computationally less demanding than the more recent ones, such as G4 [19]. Therefore, the CBS-QB3 approach is often recommended as a reference to predict the experimental results when the latter ones are not available [3]. Enthalpies of formation ($\Delta_f H^0_{298}$) for the relevant radical compounds are determined by the atomization energy method at the CBS-QB3 level of theory [22]. The theoretical rate coefficients of conventional transition state theory with an asymmetric Eckart tunneling correction [23,24] (TST/Eckart) for every elementary reaction incorporated in title reaction system are calculated. The variation of temperature increases from 500 to 2500 K, which is of interest in pyrolysis.

$$k(T) = \kappa(T)\sigma\frac{k_B T}{h}\frac{Q^{\neq}(T)}{Q_A(T)Q_B(T)}\exp(-E_a/RT) \quad (1)$$

where $\kappa(T)$ is the asymmetric Eckart tunneling correction factor, σ is reaction symmetry number, k_B is the Boltzmann constant, h is the Planck constant, $Q^{\neq}(T)$ is the partition function for the transition state, $Q_A(T)$ and $Q_B(T)$ are the partition functions for the reactants and E_a is the activation energy barrier. The total molar partition function includes translation (Q_{trans}), vibration (Q_{vib}), rotation (Q_{rot}), electronic (Q_{ele}) and torsional (Q_{tor}) partition functions ($Q = Q_{trans}Q_{vib}Q_{rot}Q_{ele}Q_{tor}$) [25]. The one-dimensional hindered rotor (1D-HR) partition function Q_{tor} is calculated by the following Eq. (2) [26].

$$Q_{tor} = \frac{1}{\sigma'}\sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad (2)$$

where σ' is symmetry number associated with that rotation, ε_i is the energy. The internal rotations of both reactant and transition state are investigated using the 1-D hindered rotor treatment. The hindrance potential for an internal rotor is obtained by relaxed potential energy scan with the step of 12° at the B3LYP/6-311G(2d,d,p) level. The overall rate coefficients of the formation of final products are deduced by using the steady-state approximation (SSA), and fitted to the modified three parameters Arrhenius expressions Eq. (3).

$$k = A \times T^n \times \exp(-E_a/RT) \quad (3)$$

All kinetic calculations are performed by implementing VKLab program [27].

3. Results and discussion

In the current study, we focus mainly the direct thermal decomposition and isomerization processes of 3-Me-1-heptyl radical, without considering the enormous amount of radical coupling processes. This is because that the thermal decomposition is a major pathway during the pyrolysis processes of hydrocarbon [9]. The global flux diagram for the pyrolysis of 3-Me-1-heptyl radical is drawn in Scheme 1. As shown in Scheme 1, the detailed mechanism mainly includes isomerization (R_1–R_6), their reversed processes (R_{-1}–R_{-6}) and the C—C bond scission reactions (R_7–R_{23}). For isomerization processes, we consider merely reversible intramolecular hydrogen atom transfer excluding CH_3 or larger radical transfer due to their relatively high barrier. For decomposition reactions, we focus just the beta C—C bond scission and exclude the beta-H elimination processes because the bond dissociation energy (BDE) of C—H bond is much higher than that of C—C bond (~12 kcal mol^{-1}) [28]. The selected geometrical parameters for some important stationary points are depicted in Fig. 1 at the B3LYP/6-311G(2d,d,p). The expectation values of $\langle S^2\rangle$ for all species contained in this reaction system are listed in Table S1. After spin annihilation, the values of $\langle S^2\rangle$ for open-shell systems very close to 0.7500, indicating that the spin contamination can be negligible at the above mentioned computation level. The standard reaction enthalpies ($\Delta_r H^0_{298}$) and enthalpies of